N
R
C

AD-A248 985
‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖

92-09542

DTIC
ELECTE
APR 15 1992
S   D
C

92 4 13 114

92-09542
‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖‖

10/87

TRIBOLOGY OF CERAMICS

Report of the
Committee on Tribology of Ceramics

NATIONAL MATERIALS ADVISORY BOARD
Commission on Engineering and Technical Systems
National Research Council

NMAB-435

National Academy Press
1988

ABSTRACT

The current state of knowledge of ceramic surface structures, composition, and reactivity is reviewed in this report. The tribological requirements of advanced mechanical systems now being developed (in particular, heat engines) exceed the capabilities of traditional metallic-based materials because of the high temperatures encountered. Advanced ceramic materials for such applications are receiving intensive scrutiny, but there is a lack of understanding of the properties and behavior of ceramic surfaces, with and without lubricants. The instrumentation and techniques available for the study of ceramic surfaces and the influence of processing on the properties of ceramics are described. The adequacy of models, ranging from atomic to macro, to describe and to predict ceramic friction and wear are discussed, as well as what is known about lubrication at elevated temperatures. From this analysis, recommendations are made for coordination, research, and development that will lead to better performance of ceramic materials in tribological systems.

COMMITTEE ON TRIBOLOGY OF CERAMICS

Chairman

BRIAN R. T. FROST, Director, Technology Transfer Center, Argonne National
Laboratory, Argonne, Illinois

Members

IAIN FINNIE, Professor of Mechanical Engineering, Department of Mechanical
Engineering, University of California, Berkeley

TRAUGOTT E. FISCHER, Professor, Stevens Institute of Technology, Department
of Materials and Metallurgical Engineering, Hoboken, New Jersey
(formerly Exxon Corporate Research Laboratory, Annandale, New Jersey)

WILLIAM A. GODDARD, III, Professor of Chemistry and Applied Physics, Arthur
Amos Noyes Laboratory, California Institute of Technology, Pasadena

STEPHEN M. HSU, Chief, Ceramics Division, National Bureau of Standards,
Gaithersburg, Maryland

MANFRED KAMINSKY, Surface Treatment Science Center, Hindsdale, Illinois
(formerly Materials Science and Technology Division, Argonne National
Laboratory, Argonne, Illinois)

BRUCE M. KRAMER, Professor of Mechanical Engineering, Department of Civil and
Mechanical Engineering, George Washington University, Washington, D.C.

DAVID W. RICHERSON, Director, Research and Development, Ceramatec, Inc.,
Salt Lake City, Utah

MILTON C. SHAW, Professor of Engineering, Mechanical and Industrial
Engineering Departments, Arizona State University, Tempe

HAROLD E. SLINEY, Senior Scientist, Surface Science Branch, NASA Lewis
Research Center, Cleveland, Ohio

WARD O. WINER, Professor of Mechanical Engineering, School of Mechanical
Engineering, Georgia Institute of Technology, Atlanta

Liaison Representatives

KENNETH GABRIEL, Director, Materials Technology Laboratory, Watertown,
Massachusetts

SAID JAHANMIR, National Bureau of Standards, Gaithersburg, Maryland (formerly National Science Foundation)

TERRY LEVINSON, Program Manager, Tribology Programs, Department of Energy, Washington, D.C.

BOBBY MCCONNELL, Wright Aeronautical Laboratory, Wright-Patterson Air Force Base, Ohio

JEROME PERSH, Staff Specialist, Materials and Structures, Office of Deputy Under Secretary of Defense for R&E (ET), The Pentagon, Washington, D.C.

NEAL REBUCK, Naval Air Development Center, Department of the Navy, Warminster, Pennsylvania

STEVEN G. WAX, Project Manager, Secretary of the Air Force, Office of Research, Department of Defense, Arlington, Virginia (formerly Defense Advanced Research Projects Agency)

Technical Advisor

LARRY FEHRENBACHER, President, Technology Assessment and Transfer, Inc., Gambrills, Maryland (formerly Institute for Defense Analyses)

NMAB Staff

Joseph R. Lane Senior Program Officer
Judith Amri, Senior Secretary

PREFACE

In the past decade, efforts to develop lighter weight, more efficient mechanical systems with components operating at temperatures ranging from subzero to 1000°C have once again identified the need to develop high-temperature tribo-materials and components. At these temperatures, modifications of traditional tribo-materials are unlikely to satisfy the need. Ceramics, either in bulk or coated forms, may be the only satisfactory materials for the tribo-elements. Unfortunately, there is virtually no science or technology base on the use of ceramics as tribo-materials at these temperatures.

In view of the importance of advanced mechanical systems applications and the need for sound design, the Department of Defense and the National Aeronautics and Space Administration asked the National Research Council's National Materials Advisory Board (NMAB) to assess the research needs and development advances necessary to provide the fundamental basis for design of extreme-temperature ceramic tribo-elements. The NMAB appointed a committee vito prescribe research and development that will lead to a better under-standing and thus to better performance of ceramic materials in tribological systems.

Committee membership was selected to cover the several disciplines that are involved in this subject area: surface physics and chemistry, lubrication chemistry, materials science and engineering, and mechanical engineering. Experimentalists, theorists, and modelers were included. The free interchange of ideas among this group and the establishment of a good interdisciplinary dialogue suggest the need for a continuation of interdisciplinary meetings in this field.

The committee proceeded to

■ Review the current state of knowledge of surface structure, composition, and reactivity in bulk and coated ceramics as related to tribological behavior

■ Evaluate the adequacy of models that describe friction and wear of bulk and coated ceramics

■ Assess fracture mechanics of ceramics as related to surface behavior

- Evaluate the adequacy of surface analytical and diagnostic tools capable of verifying and refining tribological models

- Outline the status of high-temperature lubrication of ceramics

In conducting its study, the committee perused the published literature and held committee meetings in conjunction with other specialist meetings on, or closely related to, its subject. Thus, the committee met on the occasion of the workshop on tribology sponsored by the DARPA Materials Council in La Jolla, California, in July 1985; at the American Ceramic Society's meeting on engineering ceramics at Cocoa Beach, Florida, in January 1986; and at the American Society of Lubrication Engineers meeting in Toronto, Canada, in May 1986.

Within the past few years a number of colloquia have addressed this subject, although most were concerned with tribology in general and did not concentrate on ceramics. This study differs from others in attempting to give an account of what is known scientifically about the subject and the understanding that will be required to use ceramics in advanced mechanical systems.

A topic that received much attention during the committee's deliberations is that of testing--test methods, test interpretation, and test standardization. These are topics on which there are few data, little experience, and almost no consensus. However, testing is a significant matter that deserves immediate and continuing study. As soon as more understanding and data are obtained, consideration should be given to developing standardized procedures. The goal is to permit prediction of performance; this is not possible today. The absence of a section on testing in this report reflects the lack of a basis for discussion due to the elemental state of understanding and practice, not lack of significance.

The substantial assistance of the liaison representatives, especially in formulating the problem, is acknowledged with thanks.

CONTENTS

LIST OF TABLES AND FIGURES

EXECUTIVE SUMMARY

New designs for advanced mechanical systems envision that they will operate at temperatures much higher than those encountered in conventional designs. The iron- and nickel-based alloys traditionally used in these applications cannot withstand the high temperatures contemplated. As a result, structural ceramic materials are receiving close attention for their potential use in such advanced mechanical systems, most notably in heat engines but also in advanced machine tools. To ensure that these ceramic materials achieve their best and broadest applications, a fundamental understanding of the nature, properties, and behavior of ceramic surfaces is necessary.

Because conventional lubricants vaporize or dissociate at high temperatures, it is anticipated that the ceramics, in bulk or coated form, would be used with solid inorganic lubricants. Since the adsorption and chemical reactivity of lubricants on ceramics are not the same as on metals, a basic understanding of these interactions must also be developed.

To acquire such an understanding will require a major initiative in tribology of ceramics that involves an interdisciplinary attack on the problem. New concepts in related fields combined with recent developments in surface analytical instruments emphasize the need for such an interdisciplinary approach, preferably through establishment of one or more national tribology centers at educational institutions. Such interdisciplinary centers would also encourage technolgy transfer, so that mechanical systems designers as well as ceramics producers would benefit from the knowledge gained.

Research areas that should be emphasized using an interdisciplinary approach include theoretical modeling, which would help identify the mechanisms that control performance; the relationships among structure, properties, and performance; characterization and evaluation of the performance of ceramic materials in a variety of mechanical, chemical, and thermal environments; the effect of surface modification of ceramic bodies; and novel means of lubrication under the demanding conditions anticipated in future ceramic applications.

Tribo-elements play a key role in the reliability of mechanical systems. However, the requirements for different applications vary enormously, and it

1

is not sufficient to merely state that the tribo-material must have low friction and low wear. Furthermore, the evaluation of a given material for a given tribological application is not at present a well-defined process. Although screening tests and computer simulations are conducted, full-scale prototype testing is generally required. If this evaluation process could be streamlined and made more definitive, it is possible that ceramics could be considered for additional innovative tribological applications.

Today there are essentially no theoretical guidelines for selecting ceramic materials for tribological applications. Given the large number of candidate ceramic materials and coatings that may be employed, it is extremely unlikely that ceramic tribo-systems will be optimized through exhaustive testing. Therefore, a high priority must be placed on the development of predictive models that can estimate the performance of ceramic tribo-systems based on properties that are known or that can be measured.

The tribological characteristics of a monolithic ceramic or of a surface modification are strongly influenced by the fabrication process. However, the influence of processing is difficult to study because each processing step affects the following steps differently, and thus it is necessary to assess all the associated mechanisms that might limit tribological use of the ceramic. A better understanding of the relationships among the process parameters, the physical and mechanical properties, and the resulting tribological performance is needed.

Effective lubrication to control friction, wear, and fracture of ceramic-to-metal and ceramic-to-ceramic contact interfaces is crucial to the success of many advanced technologies. A thorough knowledge of lubrication of this class of materials is therefore essential. The wide temperature range over which the materials can be used means that research issues often change as the environment and materials change with the temperature, and they also vary with different classes of lubricants-- gases, liquids, solids, and coatings. The greatest need is for an understanding of lubricant-ceramic reactivity, particularly at high temperatures. Effective delivery systems for solid or liquid lubricants also require development.

The properties of a solid are often different on the surface from what they are in the bulk. A systematic knowledge of the surface composition and reactivity of all ceramics of tribological interest could greatly assist further progress in their application. There have been rapid advances in experimental techniques for examining composition at surfaces and interfaces relevant for catalysis, tribology, corrosion, and materials synthesis, but there is as yet very little in the way of a microscopic theoretical model suitable for understanding the chemical, physical, and mechanical properties in terms of atomic-level structure and bonding concepts. A fundamental microscopic atomic-level understanding of the chemistry that controls tribology could lead to completely new strategies in designing tribological systems for extreme environments.

The microstructure of the ceramic material, the surface finish and degree of lubrication, and the nature of the applied stress all have synergistic effects that must be accounted for to obtain a basic understanding of the tribology of ceramics. Because ceramics are brittle and have less fracture

toughness compared to metals, fracture mechanics plays an important role in the tribological behavior and thus must be an integral part of any resulting model. Key factors with major influence on the fracture mechanics (and thus on the tribloligcal characteristics) are the microstructure of the material, the normal load, the geometry of the interface, the relative motion at the interface, the coefficient of friction, and the environment. These factors must be addressed individually and combined to achieve an understanding, a predictive capability, and functioning systems involving ceramics as a tribological element. There are many trade-offs between these factors. For example, excessive wear due to elastic fracture of the ceramic can be reduced by a change in interface design, use of a ceramic with a higher fracture toughness, or reduction in the coefficient of friction through better surface preparation or use of a lubricant. Further work is needed to understand the interactions of microstructure, stress, and lubrication as they apply to the tribology of ceramics, especially at elevated temperatures.

To summarize, then, the critical need to solve difficult tribological problems, particularly for ceramic components, is at the heart of such technological challenges as designing the next generation of high-performance gas turbines as well as advanced military and space systems. However, the science and technology base available is not adequate for the development of advanced mechanical systems operating at extreme temperatures. If ceramic tribo-elements are to be successfully employed in meeting such challenges, research needs to be undertaken on theoretical modeling, performance and structure relationships, surface modification, lubricants, and the effects of various chemical, mechanical, and thermal environments on tribological performance. The allocation of national resources is clearly called for to build the infrastructure needed for a multidisciplinary approach to the science and technology of tribology.

Chapter 1

OVERVIEW, CONCLUSIONS, AND RECOMMENDATIONS

For most of the past century, research and development in tribology (friction, lubrication, and wear) have been concerned with meeting the increasingly severe requirements of mechanical systems. Until the past decade, the operating temperatures of these mechanical systems were such that the tribological requirements could be met through improvements in traditional, primarily metallic-based, materials. The present trend in advanced heat engine development, however, is toward more efficient, lighter weight systems that operate at higher temperatures than current engines. Conventional iron- and nickel-based alloys are not suitable for these engines because they are too weak at the high temperatures contemplated and because the conventional organic lubricants used with these metals will dissociate or vaporize at such temperatures.

To operate at these temperatures, then, it may be necessary to use structural ceramics, in bulk or coated form, with inorganic lubricants. This combination of materials has applications in advanced cutting, grinding, and drawing tools as well as in heat engines. If ceramics and inorganic lubricants are to find extensive applications in future heat engines, machine tools, etc., in an era when computer-aided design and manufacturing (CAD/CAM) are widely applied, it is important that a better basis for ceramic systems be developed. This means that a fundamental understanding of the nature, properties, and behavior of ceramic surfaces, with and without lubricants, must be developed.

Ceramics have found tribological use for a long time, especially as dies in wire drawing, as bearings in watches, and as guides in the textile industry. When processing techniques permitted the preparation of high-performance ceramics, these materials were naturally tested for potential use in engines and other advanced machinery, but their performance was found disappointing. Ceramics often did not exhibit the excellent wear resistance that their hardness had led one to expect, and they reacted chemically with the environment and with surfaces against which they were sliding. (We will not deal with the problems of brittle fracture of the machine elements; they are significant but outside the scope of this report.) Looking back on these early attempts, we find that the disappointments were mainly due to a rather indiscriminate use of these materials. In the case of metals, a detailed

5

knowledge as to the choice of material for a given application and its proper utilization in tribological service has evolved over centuries. No such knowledge exists yet for ceramics. Whatever research has been done so far has shown that ceramics vary widely in the mechanical, thermal, and chemical properties which are relevant for their friction and wear resistance in different applications. Progress has been made. We have found that silicon nitride possesses the fatigue resistance and strength that allows its utilization in ball bearings. Such bearings perform under circumstances of rotating speeds, temperature or corrosive environments that would simply not be possible with steel. Zirconia, which exhibits a very high wear resistance in unlubricated sliding, is unsuitable for roller bearings. One of its shortcomings is its very low heat conductivity, which leads to high local temperatures. Alumina resists wear extremely well under low contact pressure but is rapidly destroyed by the large stresses encountered in ball bearings, for example. Silicon nitride seals for water and steam exhibit a performance that cannot be matched by other materials. We understand this performance on the basis of tribochemistry.

The challenge is to establish the same knowledge for the tribological utilization of ceramics that we already have for metals. We will learn to adapt to the unique mechanical, thermal, and chemical properties of these materials. It is, for example, still widely thought that the higher the hardness of a ceramic, the better its wear resistance. This argument follows the thinking that is proper to metals: hardness is the resistance to plastic deformation. Ceramics, however, wear and fail by fracture, and research has shown that toughness is the required quality for wear resistance. It can even be argued that hardness increased beyond a certain level is detrimental to wear resistance. Recent research has also shown that we will learn to exploit the unique chemistry of ceramics and develop entirely novel lubrication schemes.

In short, the research that has been performed in the recent years gives us confidence that the early disappointments do not reflect a fundamental limitation of these materials and that a technology utilizing their unique properties will evolve. We have also found, however, that the hardness of these materials does not justify their indiscriminate use; ceramics will not replace metals by better performance in all applications, they will allow us instead to develop novel technologies that would not have been possible with the more traditional materials. The remainder of this document will describe in more detail what we know about the properties of ceramics and their tribological performance and will provide specific research recommendations.

Ceramic materials behave quite differently from metallic materials. They are brittle, with a small critical crack size, and have different work-hardening and fatigue properties. Likewise, the adsorption and chemical reactivity of lubricants on ceramics are quite different from those of metals. Because traditional liquid lubricants are not satisfactory for ceramics at high temperatures, solid inorganic lubricants may be the only materials that can be used. A serious need for basic understanding, as well as development and experience in the use of ceramics as high-temperature tribo-elements, must be satisfied if numerous advanced mechanical systems are to be successfully developed. This understanding should cover, in a continuous, connected way, a view of ceramics ranging from the atomic level

through the microstructure to the bulk. At this last level, there is a direct linkage to design methods, provided the appropriate materials property data are available to the designer.

The tribology of ceramics is strongly influenced by interactions between the microstructure, interface design, stress distribution, surface condition, temperature, and application environment. There are many trade-offs between these factors. For example, excessive wear due to elastic fracture of the ceramic can be reduced by a change in interface design, use of a ceramic with a higher fracture toughness, or reduction in the coefficient of friction through better surface preparation or use of a lubricant. Resolution of chemical effects may be more difficult and may require a major design or material change. Other options include surface coatings (plasma spray, chemical vapor deposition, physical vapor deposition) or surface modification (ion implantation, ion mixing, laser mixing). These are discussed in a separate chapter.

There is considerable synergism among the factors that influence the tribology of ceramics. Temperature typically increases the effects of atmosphere and impurities and can lead to localized pressures that further modify behavior. Corrosion reactions reduce the strength and hardness of the material and increase the susceptibility to mechanical surface damage during sliding contact.

The methodology is now evolving to develop models of wear behavior from the atomic level (quantum chemistry approach), through microstructural models that involve dislocation theory and microscopic-level fracture mechanics, to the continuum-level linear elastic fracture mechanics approach. A logical linking of such models would be desirable.

CONCLUSIONS

Designs for some advanced military and space systems call for ceramic tribological elements to operate at extreme temperatures. This is despite the fact that there is no significant scientific understanding to permit selecting ceramic tribo-elements or for identifying the failure modes. Incremental improvements are insufficient to assure dependable operation of the systems. The science and technology base available is not adequate for the development of advanced mechanical systems operating at extreme temperatures, where metals cannot be used.

At the same time, program managers and technical policy-makers lack awareness of the critical function required of parts such as ceramic bearings and of the meager knowledge base for selecting and optimizing a ceramic system. Therefore, a major initiative in tribology of ceramics is required, particularly one involving an interdisciplinary attack on the problem.

The following are a few of the broad issues that came out of the study.

• *Scientific and Engineering Data:* Although there have been substantial recent advances in the science of tribology in general, including ceramic tribology, many new concepts have been developed in related fields. There has been significant development of the tools of science, particularly

surface analytical instruments. The time is ripe, therefore, to encourage interdisciplinary work. The establishment of tribology centers in government and industrial laboratories is highly recommended. The establishment of one or more interdisciplinary national centers of tribology at educational institutions in the United States is also needed. Furthermore, because the design fraternity is not well acquainted with the facts that are known, this is a field in which technology transfer needs encouragement. Recent initiatives by the Department of Energy are a good step in this direction. There needs to be a greater awareness among mechanical system designers and the producers of ceramics about the unique properties of ceramics in tribological applications if success in their utilization is to be ensured.

- *Theoretical Modeling:* Further development is needed of models at both the atomic level and the macroscopic level and their extension toward each other in size scale to achieve an understanding that would permit the designing of materials. With such scientific understanding it should be possible to identify the controlling mechanisms in the performance of ceramics used as tribo-materials.

- *Performance and Structure Relationships:* Basic to understanding of mechanical properties of solids is an appreciation of the structure-property-performance relationship. This needs to be clarified both for solid ceramics and for ceramic coatings. With such a comprehension it becomes possible to develop and evaluate novel techniques for the production of bulk and coated ceramics.

- *Surface Modification:* In addition to production of massive ceramic bodies, work on chemical or structural modification of the ceramic surface has been a promising area of development, and this work should be continued.

- *Lubricants:* Innovative concepts for incorporating or generating solid, liquid, or gaseous materials in the surface to perform the function of a lubricant are badly needed and should be actively pursued.

- *Evaluation:* Much more data are needed on tribological performance in various chemical, mechanical, and thermal environments. For such data to have general usefulness, careful characterization, especially of the material, is mandatory. In addition, development (and to the extent possible, standardization) of tests is needed.

RECOMMENDATIONS

Specific recommendations relating to needed work in various aspects of the science of tribology of ceramics are given at the ends of chapters. They are reproduced here to provide an overview.

Influence of Fabrication

Tribological studies of ceramics must consider the variables that might arise due to the fabrication process and incorporate these into the evaluation procedure for the tribological study. As a minimum, the ceramic

should be well characterized prior to the tribological study. Specifically, this should include bulk chemistry, microstructure, surface structure (asperities, residual stress, cracks, etc.), pore distribution, strength, elastic modulus, Poisson's ratio, and fracture toughness.

Research is needed to acquire more understanding of the relationships among process parameters (and the resulting structure), physical and mechanical properties, and the resulting tribological performance. This not only would permit the optimization of a given process, but also would provide a basis for selecting from alternate fabrication techniques.

Lubrication

In the area of ceramic lubrication, the most urgent need is to develop an effective lubrication system so that ceramics can be utilized effectively. To accomplish this, research in several areas needs to be addressed:

Lubrication Mechanisms

■ Low temperature (bulk temperature) applications are going to create the largest short-term markets for structural ceramics. The chemical reactivity between hydrocarbon structures with ceramic surfaces needs to be defined. The mechanisms of reaction and rates of reaction under boundary lubrication conditions should be studied to examine the structural effects, functional group influence, and the physical properties effects.

■ Surface forces at ceramic surfaces need to be measured. The additional double layer forces at ceramic surfaces will effect adsorption, lubricant-substrate adhesion, wetting, and reactivity.

■ Lubrication mechanisms of solid lubricants at high temperatures need elucidation. Effects of diffusion, segregation, reactions, degradation on adhesion, and surface protection need careful study. The formation of new phases, reaction products at high temperatures, with and without tribo-contacts, needs to be defined.

■ Thermodynamic equilibrium of phases and solubilities of the lubricant and substrate needs to be experimentally determined and subsequently predicted by models.

■ Degradation mechanisms of lubricants and their influence on friction and wear over the temperature ranges should be studied.

Lubricant Development

■ Element-specific chemistry based additives that provide friction and wear control through the formation of protective friction and wear control through the formation of protective films need to be developed.

■ High-temperature antioxidants that can survive 400°C for a short period of time should be developed. Various mechanisms may be operative at this temperature.

- For heat engine applications, high temperature (400°C) ashless dispersants and acid neutralizers are needed.

- Novel compositions in synthesizing high-temperature liquid lubricant need to be explored.

Lubricant Delivery and Disposal Research

- Vapor phase-deposited lubricants for short duration protection constitute a very attractive concept. Functionality, reactivity, deposit control, and reaction mechanisms need to be systematically investigated.

- Impregnation of lubricants into the materials substrate by coatings, physical vapor deposition, ion beam mixing, and self-lubricating composites should be explored.

- Spent lubricant and wear debris will be deleterious to system durability. Mechanical design changes as well as chemical means in removing them may be critical to the lubricant selection.

In ceramic lubrication research fundamental information is lacking. While the technology of metal lubrication has matured, detailed mechanisms are not fully understood. Thus information transfer from existing technologies to ceramic lubrication may be very few. A systematic effort is defining the surface energy, surface reactivity, and surface composition of simple single crystals with different molecules under different environmental factors needs to be established.

Chemistry of Ceramic Surfaces

- A systematic knowledge of the surface chemistry of ceramics (i.e., their surface composition, adsorption, surface reactions) must be acquired over a temperature range extending from 200 to approximately 1400°K. This is a prerequisite for the formulation of lubricants and additives.

- The phenomenology and mechanism of tribochemistry of ceramics, defined as the chemical reactions induced or modified by friction, must be studied in the environment and in contact with the lubricants expected over the whole temperature range to be encountered in practice.

- Surface characterization methods capable of detecting water and hydrogen must be further developed because of the widespread occurrence of surface hydration of ceramics.

- Surface morphology and structure must be determined with very fine lateral resolution because of the importance of stress concentrations in the contact of hard bodies.

- Surface crystallography must be studied as modified by friction. Toughening and embrittling phase transformations have been discovered and modify the friction behavior.

■ A better understanding of the hardness and toughness of ceramic surfaces must be obtained because of their influence on contact geometry and stresses.

■ The influence of adsorption on crack initiation and crack propagation plays an important role on wear and lubrication of ceramics. These phenomena demand an exhaustive experimental and theoretical study.

■ More progress must be made in the nondestructive detection of near surface flaws and cracks because the latter determine the reliability and wear resistance of ceramics and could vastly improve the manufacturing of these materials.

Surface Characterization

■ Investigate improved methods for detecting light elements, especially hydrogen and its chemical radicals and compounds (e.g., hydroxyl, water, etc.).

■ Develop techniques for in situ analyses of ceramic wear surfaces during tribological experiments.

■ Investigate techniques that do not require a vacuum (e.g., optical techniques such as FTIR, Raman, etc.).

■ Explore methods such as the use of a small spot electron spectroscopy for chemical analysis (ESCA) device with an atmosphere working chamber connected to a vacuum analytical chamber via interconnect locks for rapid transfer of specimens from working environments to an analytical chamber within the same apparatus.

Fracture and Wear of Ceramics

■ To provide a basis for fundamental understanding, we need to establish a quantitative equation for the mechanical wear of ceramics. This would include (a) a theoretical description of wear by microfracture according to fracture mechanics and contact stress distributions, (b) a determination of the relative importance of toughness and hardness in wear, (c) establishment of the load dependence on wear in elastic contact and fracture, and (d) a determination of the role of microstructure on the resistance to wear by fracture.

■ Additional fundamental understanding also needed is a quantification of the microfracture in wear as a function of material characteristics and contact stress conditions. This includes (a) effect of microstructure on fracture of the material, (b) relation of the microstructure to the scale of the wear process, (c) relation of the scale of toughening components to wear, and (d) stress concentration at micropores.

Modeling of the Chemical and Tribological Properties of Ceramic Surfaces

To establish a basis for atomic-level simulation of the fundamental surface processes responsible for friction, adhesion, wear, and abrasion, the following is recommended:

■ A major thrust is needed in the development of theoretical methods relevant to tribology and ceramics. This would involve quantum chemistry studies of the fundamental forces in model systems, development of force fields suitable for atomic-level simulations, and simulations of realistic models and tribological systems.

■ Focus fundamental studies (both theoretical and experimental) on a series of standard systems that will serve as benchmarks for comparison between theory and experiment and between the work of different laboratories.

Chemical Interaction Among Ceramic Components

It is likely that the chemical interactions among ceramic components will ultimately determine their performance in practical applications. Therefore, given the current lack of theoretical guidance in materials selection, it is important to begin the development and evaluation of theoretical models that can be used in design. The following steps are recommended:

■ Undertake a study of available metal-ceramic and ceramic-ceramic phase diagram data to develop semi-empirical compatibility criteria for ceramic materials.

■ Begin to develop quantitative, analytical friction and wear models based on the chemical affinity between sliding surfaces as evaluated by chemical thermodynamic calculations.

■ Undertake test programs on well-characterized materials to provide reliable data for comparison to model predictions. Both ceramic-ceramic and metal-ceramic systems should be included.

■ Incorporate the modification of contact stresses by lubricants in the boundary, mixed and hydrodynamic lubrication regimes into theories of friction and wear.

Chapter 2

TRIBOLOGICAL NEEDS

Material requirements for tribological elements are among the most
severe of all mechanical systems. Both bulk and surface properties are
important. Mechanical, thermal, and chemical properties are all signifi-
cant for the successful production and application of tribo-elements. In
addition, materials used as tribo-elements must be capable of being shaped
with high accuracy in form as well as to a fine surface finish. The material
must also be capable of maintaining long-term stable geometry and integrity.

In a mechanical system, the tribo-element must be a structural element
the surface of which is subjected to high local stresses (to 3 GPa) and high
local temperature rises (hundreds of degrees) above the bulk temperature.
The surface also experiences chemical interaction with the environment. The
most desired chemical interaction is for the surface reaction to result in
a useful (protective) tribological film formed at an acceptable rate. One
cannot generalize about the tribological material requirements because those
requirements vary with the type of tribo-element and the mechanical system in
which it is to be used. Lip seals, brakes, or sleeve bearings
have different requirements from rolling element bearings, cams, or gears.
Tribo-elements that are to operate in precision instruments have different
requirements from those used in a minimum cooled internal combustion engine
or ship shaft seal. Simply stating that the tribo-material must have low
friction and low wear is not of value in understanding the tribological
material needs.

The level of understanding of tribo-material performance required is
high because tribo-elements play a key role in determining the reliability of
mechanical systems. In addition, quality control and nondestructive testing
technology must be developed for new materials when they are to be used in
tribological applications.

Tribological evaluation of materials is currently an art at best and
certainly not a science. As was clearly developed in the 1985 DOE workshop
on tribo-testing, there is no simple measurement to be made that will qualify
a material as suitable for a given tribological application (Yust et al.,
1986). There is a great need to develop the technology of tribo-testing to
provide the full spectrum of tribo-material evaluation, from material

13

screening to full simulative evaluation, all with relevance to the intended application area. Numerous screening tests are used to define the possible suitability of a given material for a particular tribo-application. More appropriately, reasonably complete systems simulations of the application are conducted to build confidence in the appropriateness of a material selection. In the final analysis, full-scale prototype testing is usually required to establish confidence in a new material for a tribological application. Tribological materials requirements cannot be meaningfully specified independent of the application.

The use of ceramics as tribo-materials is not new. Ceramics have long been used successfully as tribo-elements in precision mechanical instrumentation such as chronometers. These applications are not severe in a tribological sense. In the past decade, ceramics have come into general use in metal-cutting tools, both as coatings and as monolithic components. Such applications are among the most severe of all tribo-elements, but the life requirements are generally short compared to tribo-elements in other mechanical systems. Ceramics are also used as seal faces and electrical brushes. Ceramics will continue to be considered and evaluated for tribo-applications whenever their use seems potentially advantageous.

An important question for consideration is whether there are other tribological applications with particular requirements that might be satisfied by ceramics. Tribo-elements are generally made of metals and/or solid polymers. In what ways are the properties of ceramics different from those of metals and polymers, ways that might permit ceramics to be used advantageously in tribological applications? Ceramics are characterized by higher rigidity and frequently by greater high-temperature strength and stability than are metals or polymers. Their density and thermal conductivity are lower than those of metals but higher than those of polymers. Finally, ceramics are made of readily available raw materials, a quality that the Japanese have found attractive. The raw material difference between ceramics and high-performance metals is more a question of anticipated availability of strategic materials than of economics, because, in selecting tribo-materials, performance is generally more important than cost.

On the basis of these characteristic differences between ceramics and other tribo-materials, many potential applications for ceramics are apparent. Perhaps the most obvious is the need for tribo-materials for high-temperature thermal systems development, such as the minimum-cooled diesel engine and high-performance turbine engines. The lower density of ceramics suggests using them in high-DN* rolling element bearings to reduce centrifugal forces between the rolling element and the race. The higher elastic modulus indicates potential application wherever high stiffness is important in mechanical systems such as machine tools and mechano-optical positioning systems. The different chemical properties suggest the use of ceramics as tribo-materials in various chemical processing systems and in other hostile environments. The different chemical properties, however, point to the possible need for new lubricants to be used with ceramics and to

---

*DN is the product of the bearing bore diameter (D) in millimeters times the rotational speed (N) in revolutions per minute and is a measure of bearing performance limitations in large and/or high-speed systems.

the possibility of unanticipated surface reactions with the environment, which may be either beneficial or deleterious. While future applications cannot all be identified, certainly tribological needs that might be satisfied by ceramics are numerous.

In the total scheme of mechanical system development or operation, tribo-elements are not the primary concern of those responsible but are part of the necessary, but not sufficient, supporting technology often taken for granted. The acceptability criteria for tribo-elements, including the choice of material of construction, are usually based on reliability, wear, friction, and cost, in that order. Because the cost of existing tribo-elements is usually small when compared to the total mechanical system cost, the economics are important only after the reliability, wear, and friction of the tribo-element are acceptable. The support role of tribo-element technology suggests that the tribological needs can be divided into two broad categories: (a) tribological needs in existing commercially available mechanical systems and (b) tribological needs in new mechanical system concepts under development.

The tribological needs in existing mechanical systems that are commercially available are many and varied but seldom imperative in nature. Engineers responsible for these systems are frequently on the lookout for tribo-elements that give a significant improvement in one or more of the five areas (reliability, durability, wear, friction, and cost) without any significant penalty in any of the other areas. Examples are numerous where improved reliability, longer wear life, or reduced friction would be welcome in existing mechanical systems, even if no other direct benefit was obtained for the system. In other cases, improved tribo-elements will permit significant primary advances in the existing mechanical system. Examples of these advances include higher DN rolling element bearings permitting greater thrust-to-weight ratio in aircraft turbine engines by allowing higher shaft speeds; improved metal-cutting tools permitting higher production rates; better workpiece dimensional control in manufacturing; and lighter weight, lower friction tribo-materials that result in better fuel economy in automotive engines. In this last category the introduction of new tribo-materials such as ceramics may permit significant advances in the evolution of existing mechanical systems.

In the development of advanced mechanical system concepts, tribo-elements and tribo-materials may be among the primary pacing technologies. Recent Department of Energy and Defense Advanced Research Projects Agency studies have delineated the tribological needs in advanced heat engine development (Fehrenbacher and Levinson, 1985; Fehrenbacher and Oelrich, 1984) and in advanced military system development (Fehrenbacher and Oelrich, 1984). In the development of new concepts for heat engines, tribo-elements, primarily in the form of seals, have historically been the pacing technology. This factor was apparent 50 years ago in the development of the aircraft gas turbine engine (gas path seals) and is still true today (Fehrenbacher and Levinson, 1985; Fehrenbacher and Oelrich, 1984).

Table 2-1 lists the current limiting tribological components for advanced heat engines. In some cases (e.g., the automotive turbine, Wankel, and Stirling engines) the tribo-element development has been the pacing technological factor for the last 2 to 3 decades. The ring-cylinder

tribology has been the pacing technological factor for the low-heat rejection (adiabatic) diesel for a decade. As recently as 1984, reports of engine testing in the low-heat rejection engine program indicate that tribology problems, particularly in the upper cylinder region, still present formidable development hurdles (Johnson, 1984). The low-heat rejection diesel program has been under way for over a decade, and concern is growing among engine developers and government officials that the full potential of the advanced engine will never be realized unless associated tribology advancements are forthcoming (Fehrenbacher and Levinson, 1985).

TABLE 2-1 Limiting Tribo-Components for Advanced Heat Engines

Engine Type	Critical Components	Tribological Limitation
Automotive turbine	Rotary regenerator seals	High temperature, low wear, solid lubricated materials
Rotary Wankel	Apex seals	Low wear, solid lubricated materials
Stirling	Piston-cylinder seals, dry lubricated crank-shaft bearings	High temperature, low wear, solid lubricated materials
Diesel	Cylinder kit	High-temperature liquid lubricants

Source: Fehrenbacher and Levinson, 1985.

The Institute for Defense Analyses report for the Defense Advanced Research Projects Agency (Fehrenbacher and Oelrich, 1984) found that a number of advanced military systems under development had critical tribological needs that were pacing the development of those systems. Figure 2-1 shows a matrix of these systems and the associated tribological needs where solid-lubricated ceramics technology is believed to be essential or desirable to the system development.

An important fact shown by Figure 2-1 is that the use of nonmetals or nonmetallic surfaces is desirable or essential for most applications. The extreme environmental conditions in which these tribo-systems must function strongly favor or demand development of solid-lubricated ceramic tribo-systems. The anticipated greater fatigue and wear resistance and enhanced chemical and dimensional stability are inherent advantages of tribo-elements made from ceramics. However, the technology base for solid-lubricated ceramics is so rudimentary for many of these applications that substantial improvement in understanding of tribo-chemical and tribo-mechanical

17

TRIBOMATERIALS REQUIREMENTS (columns: Regenerator Seals, Cruise Missile Bearings, Cryocooler Bearings, Cryocooler Seals, Satellite Bearings, Satellite "Wheels", Turbopump Bearings, Turbopump Seals, Homopolar Generator Brushes, Homopolar Generator Seals, Transmission Friction Elements)

Requirement	Regen. Seals	Cruise Missile Brg	Cryocooler Brg	Cryocooler Seals	Satellite Brg	Satellite Wheels	Turbopump Brg	Turbopump Seals	Homopolar Gen. Brushes	Homopolar Gen. Seals	Transmission Friction Elem.
SOLID LUBRICATION					DESIRABLE	DESIRABLE					
ADVANCED LIQUID LUBRICATION					DESIRABLE	DESIRABLE					
HIGH TEMPERATURE MATERIALS											
PROPELLANT COMPATIBILITY											
NON-METALLIC			DESIRABLE		DESIRABLE	DESIRABLE	DESIRABLE				
ELECTRICALLY CONDUCTING											
CRYOGENIC WEAR MATERIALS											

☐ ESSENTIAL ▨ DESIRABLE

FIGURE 2-1 Tribo-materials requirements for critical applications, indicating need for solid-lubricated ceramics technology (Fehrenbacher and Oelrich, 1984).

behavior will be required. Significant payoffs could result from the development of solid-lubricated ceramic materials systems (Fehrenbacher and Oelrich, 1984).

There is a major need for the development of a science and technology base in relation to the use of ceramics as tribo-materials. There simply is too little understanding and experience in the field to expect satisfactory performance of tribo-elements in advanced and extreme-temperature mechanical systems. Ceramics cannot be successfully employed simply by substituting them for other tribo-materials. Many mechanical systems currently under development will not be successful unless the science and technology base of ceramic tribo-materials is established.

Technology transfer is also a major need in this field. The results of the very limited generic research and development studies that have been done, and the knowledge that must be developed, need to be transferred in an understandable fashion to mechanical systems designers. The unique characteristics of ceramics lend promise to the potential use of ceramics to further the development of several mechanical systems. However, the behavior of ceramics in tribo-systems must be better understood, and that

understanding must be conveyed to the mechanical system designer in a usable form before the potential of ceramic tribo-elements can be attained.

In addition, there is, on the part of major advanced mechanical systems planners and managers, a serious lack of awareness of the importance of tribology to the successful development of those systems. Resources are not made available to develop the critical tribo-technology at the beginning of a project. When the inevitable problems are encountered, the seriousness of the associated lack of knowledge and human resource basis is usually not recognized. This lack of awareness has been a historical problem in the field of tribology, resulting in a totally inadequate human resource base and knowledge base in this important field. Tribology is a significant enabling technology throughout virtually all fields of engineering, yet it is rare that an engineering student at any level is exposed to the field. There is also relatively little tribology research and development activity in the national laboratories and in most industry. A major need in tribology in general, and the tribology of ceramics in particular, is the need to establish a human resource base within which knowledge and experience in this important enabling field of technology can be developed.

REFERENCES

Fehrenbacher, L. L., and T. M. Levinson. 1985. Identification of Tribo-logical Research and Development Needs for Lubrication of Advanced Diesel Engines. Report PNL-5537, UC-95. Richland, Washington: Battelle Pacific Northwest Laboratory.

Fehrenbacher, L. L., and I. C. Oelrich. 1984. Opportunities in Future Military Tribology Research and Development. IDA Paper P-1805. Alexandria, Virginia: Institute for Defense Analyses.

Johnson, D. R. 1984. Ceramic Technology for Advanced Heat Engines Project: Semiannual Program Report, October 1983-March 1984. Report ORNL/TM-9466. Oak Ridge, Tennessee: Oak Ridge National Laboratory.

Yust, C. S., S. M. Hsu, and T. M. Levinson. 1986. Ceramic Tribology: Assessment of Needs in Measurement Methods and Standards. ORNL/TM-9921. Oak Ridge, Tennessee: Oak Ridge National Laboratory.

Chapter 3

INFLUENCE OF FABRICATION ON BEHAVIOR OF CERAMIC TRIBO-ELEMENTS

Chapter 2 provided an overview of tribological needs and key application categories. Chapters 3 through 9 present further details on tribology needs, background information for specific aspects of tribology, and recommendations that should be considered for future tribology program planning. This chapter concentrates on a general discussion of the influence of fabrication of ceramic tribo-elements and identifies some important considerations for fabrication and characterization.

The tribological characteristics of a monolithic ceramic, a composite ceramic, or a surface modification are strongly influenced by the fabrication process. This chapter discusses the steps of fabrication, the different fabrication approaches, and the potential effects on the tribological behavior. Fabrication of the bulk ceramic is discussed first, followed by discussion of the coating and surface-modification approaches.

MONOLITHIC CERAMICS

For the purposes of this document "monolithic ceramic" refers to the use of a bulk noncomposite ceramic material as the tribological surface, rather than the use of a coating or a surface modification. The ceramic can either constitute the whole component or an insert.

The tribological characteristics of a ceramic material can be strongly influenced by the fabrication process. Table 3-1 lists the steps in fabrication of a ceramic material, identifies factors that might influence the tribology, and suggests associated mechanisms that must be assessed that might limit tribological use of the ceramic.

The processing steps listed in Table 3-1 are not independent of each other. Each affects the others. For instance, the composition strongly affects the densification kinetics and the powder preparation strongly influences the forming and densification parameters. This interdependence increases the difficulty of study of the influence of processing on tribology; it places stringent demands on the researcher to carefully characterize the ceramic material for variations that may arise due to

processing. Characterization of the ceramic prior to tribological testing should include surface and bulk evaluation of chemistry, phase content, and microstructures as well as measurement of density, strength (including critical flaw size), hardness, fracture toughness, and surface finish (including SEM or replica TEM to show the distribution and nature of asperities).

The following sections discuss key considerations for each of the processing steps listed in Table 3-1.

TABLE 3-1   Fabrication Factors and Their Influence on Tribology

Process Step	Factors Influencing Tribology	Potential Limiting Mechanisms
Powder preparation	Final grain size; homogeneity; final surface finish; critical flaw size	Asperities; strength; spall sites
Forming	Homogeneity; critical flaw size; residual stress; dimensional tolerance	Geometry; strength
Densification	Grain size; critical flaw size; dimensional tolerance	Geometry; strength
Finishing	Surface finish; critical flaw size; friction and wear coefficients	Asperities; strength; surface chemistry

Powder Preparation

The first major step in processing is powder preparation. As-received powders generally do not have the optimum particle size and distribution characteristics needed to be formed and densified to optimum properties. The powders typically are milled or classified, during which additional impurities are picked up that may affect the composition or become inhomogeneities, which reduce strength. The powder preparation influences the final grain size, the surface finish that can be achieved, and the material strength.

Forming

The forming step involves compaction of the powder into a preform that can be densified. An important criterion is to achieve as close packing of the particles as possible. Organic additives are used as lubricants,

compaction aids, and binders. Concerns here are homogeneity, retained residues from organics, residual stresses, and dimensional tolerances.

A variety of forming techniques are available. The most common are pressing, slip casting, extrusion, and injection molding. Each has many parameters that must be carefully controlled to achieve a reproducible product. Each can result in defects unique to that specific forming process. A tribology researcher must therefore be aware of the forming process by which test specimens or tribo-elements were fabricated and must be knowledgeable of the types of defects that are inherent to that process. Discussions of the forming processes (and other process steps) and potential defects are available in the literature (Mangels and Messing, 1984; Richerson, 1982; Onoda and Hench, 1978; Wang, 1976).

Densification

Densification involves the bonding together of the individual particles into a strong, pore-free ceramic body. This is achieved at high temperature. The temperature depends on the material and the nature of the sintering aid additives and impurities. Alumina is normally densified in the range 1400 to 1700°C. Silicon carbide typically requires a temperature greater than 2100°C.

The success of the densification step is determined by control of furnace parameters (temperature, pressure, atmosphere, cycle time, fixturing, etc.) as well as by the quality of the starting powder, powder preparation, and forming. Defects from the prior processing steps are usually not removed by the densification step.

The composition and sintering aid strongly affect the densification step and the resulting properties of the ceramic. Liquid-phase sintering leaves a concentration of the sintering aid plus impurities as a thin film between grains of the baseline ceramic. This microstructural inhom :eneity will have a different tribological response than will a uniform microstructure derived from solid-state sintering. This does not mean that the solid-state sintered material will work better. It just means that the tribology researcher needs to be aware of the sintering mechanism and must characterize the material for any microstructural inhomogeneity that might affect the tribological behavior.

The grain boundary phases are examples of short-range composition variations that are distributed throughout the material and thus have a bulk effect. Some inhomogeneities are more random in distribution and result from isolated inclusions (present in the starting powder or picked up during processing), isolated large pores (arising from agglomerates in the powder and poor particle packing during forming), or irregular grain growth. These intermittent inhomogeneities may affect the tribology, but they definitely affect the mechanical properties.

Shrinkage occurs during densification. The amount of shrinkage is the difference between the total porosity in the powder compact (after removal of organic binders, etc.) and the final porosity after sintering. Linear shrinkage typically is 15 to 20 percent. This large amount of dimensional

change makes it difficult to fabricate a ceramic part within close tolerances without a finish machining operation.

Surface-connected porosity is generally detrimental. It increases the coefficient of friction, it provides sources of stress concentration in a tensile stress field, and it provides points of weakness that can even produce crack initiation in a compressive stress field. The latter case requires further explanation. Solid ceramic bridges between pores can collapse or crack. When these link together a wear particle will separate. The situation will be worse under a sliding contact load where both compression and tension occur, and it will be still worse if the sliding load is cyclic.

Finishing

Ceramic parts for tribology systems generally require final grinding and/or lapping to achieve the necessary dimensional and smoothness tolerances. The grinding operation can (and generally does) introduce surface cracks that dominate the fracture mechanics characteristics of the ceramic. The grinding and lapping also determine the asperity distribution, which partially determines the coefficient of friction. Grinding and lapping can also modify the surface composition and phase distribution and thus alter the response of the ceramic to a lubricant or other aspect of the tribology environment.

Microstructure affects the mechanical aspects of tribological behavior. Grain size and surface-connected porosity determine the surface finish that can be achieved in the as-fired material. Internal porosity affects the surface finish that can be achieved by grinding and polishing. These microstructural factors influence the coefficient of friction, which in turn partially determines the level of stress at the material surface during sliding contact. The cohesion and morphology of the microstructure determine the strength and fracture toughness of the ceramic and its resistance to damage by the applied stress.

CERAMIC COMPOSITES

Tribo-elements are often exposed to mechanical or thermal stresses in addition to withstanding the wear, corrosion, or other conditions associated with the tribological duty. Monolithic ceramics may not have the strength and fracture toughness to survive these stresses. Increased emphasis in recent years has been to develop ceramic matrix composites that have higher strength and fracture toughness compared to monolithic ceramics.

A variety of composite approaches are being developed: (1) dispersed ceramic particles, (2) dispersed ceramic whiskers, (3) long fiber reinforcement, (4) precipitation, and (5) ductile metal phase. Each of these results in a microstructure containing two or more phases. These phases affect both the chemical and mechanical tribological behavior. For example, each phase will have different chemical interactions with the contacting tribo-element, the environment, and the lubricant. Similarly, each phase will have a different elastic modulus, Poisson's ratio, and coefficient of thermal expansion and have a different mechanical response to the contacting

tribo-element. For example, each intersection between two phases may act as a micro-asperity under loading and result in increased friction and increased surface stress.

COATING AND SURFACE MODIFICATION

A monolithic ceramic may not have the optimum surface characteristics for a specific tribology application. Coatings or surface modifications either on the ceramic or on a metal or cermet substrate can often provide advantages in corrosion resistance, impact erosion resistance, adhesive and/or abrasive wear resistance, and high-temperature ("solid" film) lubrication.

The coating or surface-modification approach also offers several advantages in the synthesis of high-performance materials. One advantage is the ability to optimize independently the properties of the coating material and those of the base material for a given application. This often results in novel layered materials that are superior to monolithic ceramics in their performance. A second advantage is the ability to maintain close dimensional tolerances of the coated workpiece, since very thin coatings (of the order of a few micrometers) are often sufficient for a given application. Another advantage is the saving in costs in using expensive special materials only for thin coatings and not for the synthesis of bulk materials. Such savings also help in the conservation of strategically critical materials. Finally, it is often more advantageous to recoat a worn part than to replace it. In view of these advantages it is not surprising that ceramic coatings have found wide commercial acceptance.

As is the case for monolithic ceramics, the characteristics (e.g., composition, microstructure), properties (e.g., strength), and tribological behavior (e.g., friction, wear) of ceramic coatings and surface-modified ceramics can be strongly influenced by the fabrication process. This points to an opportunity for the production of advanced ceramic coatings and surface-modified ceramics with significantly improved tribological performance through proper choice of processes and an optimization of process parameters. Unfortunately, present understanding of the influence of processing on the relationship of structure, property, and tribological performance is too fragmentary to provide sufficient guidance for an optimization of process parameters.

The following sections give summaries of (a) the major considerations in selecting processes for ceramic coatings and for modifying ceramic surfaces and (b) the major processes and major processing steps.

Considerations in Selection of Processes for Ceramic Coatings and for Modifying Ceramic Surfaces

The selection of a particular deposition process or surface-modification process depends on several considerations. A prime consideration deals with the characteristics and properties of the coating one wants to obtain for a given application. Some of the characteristics and properties of ceramic coatings that are often considered to be desirable are these:

- Good adhesion
- Precise stoichiometry (negligible contamination)
- Uniform thickness
- High dimensional stability
- High strength
- High fracture toughness
- Internal stresses at acceptable levels
- Controlled density of structural defects
- High thermal shock resistance
- High thermal stability
- High resistance to wear and creep
- High resistance to oxidation and corrosion
- Adequate surface topography

One typically chooses a coating process to obtain certain combinations of characteristics, properties, and performance. Additional considerations that can influence the selection of a coating process include (a) the purity, state (gaseous, liquid, or solid), and type and toxicity of the material to be deposited; (b) the deposition rate; (c) the tolerable power density on the substrate during deposition; (d) the maximum temperature the substrate is permitted to reach during the coating process; (e) the substrate treatment needed to obtain good coating adhesion; (f) the selectivity of the process in depositing certain materials and not others; (g) adequate control of the major process parameters that govern the deposition process in order to ensure the reproducibility of the coating deposition; (h) the complexity and availability of the coating facility; and (i) the overall cost.

It would be desirable to be able to select a process on the basis of well-established relationships between coating process parameters and coating characteristics and properties, and in turn between the characteristics and properties and the coating performance for a given application. Unfortunately, for most processes such relationships are either inadequate or do not exist at all. Therefore, one is often forced to rely on experience gained through trial and error. Work is in progress to establish such relationships for certain processes—for example, for ion-assisted deposition processes (i.e., ion beam- or plasma-assisted physical vapor deposition). However, in view of the existing widespread use of coated machine components and the projected future requirements for components with advanced coatings, it is clear that more work along these lines is urgently needed.

Processes for Ceramic Coatings and for Modifying Ceramic Surfaces

Many different processes are in use for fabricating ceramic coatings and monolithic ceramics. Table 3-2 lists some processes according to category and class they have been assigned to. For ceramic coatings, the categories include processes that require the surfaces to be exposed to (a) low-pressure gases (vacuum), (b) elevated gas pressure, and (c) liquid solutions and suspensions. The surface-modification categories include processes that require (a) energetic particle implantation (ion implantation), (b) densification and glazing of coatings through electron and/or laser beams, (c) chemical surface reactions, (d) thermal diffusion, (e) chemical etching, and (f) mechanical grinding and polishing.

TABLE 3-2 Selected Processes for Production of Ceramic Coatings and for
Modification of Ceramic Surfaces

Process Category	Process Class	Process
1. Ceramic Coatings		
Low gas pressure (vacuum) processes	Chemical vapor deposition (CVD)	Pyrolysis; reduction (plasma-assisted); decomposition (plasma-assisted); polymerization (plasma-induced)
	Physical vapor deposition (PVD)	Evaporation (reactive, plasma-assisted); sputtering (reactive, plasma-assisted); plasma-arc (random, steered); ion beam-assisted codeposition
	Low-pressure plasma spraying	Plasma discharge spraying
Processes at elevated gas pressures	Plasma spraying	Plasma arc spraying
	Flame spraying	Combustion flame spraying
Liquid phase epitaxy processes	Wetting process	Dip coating (e.g., Sol-Gel); brush coating
	Spin-on coatings	Reverse-roller coating
Electrochemical processes	Electrolytic deposition	Cation deposition
	Electrophoretic deposition	Charged collodial particle deposition
	Anodization	Anion oxidation in electrolytes
	Electrostatic deposition	Charged liquid droplet deposition
2. Modification of Ceramic Surfaces		
Particle implantation processes	Direct particle implantation	Energetic ion or atom implantation in solids
	Recoil particle implantation	Recoil atom (ion) implantation in solids
Densification and glazing processes	Laser beam densification and glazing	CW-laser power deposition; pulsed-laser power deposition
	Electron beam densification and glazing	Energetic electron beam power deposition
Chemical reaction processes	Gaseous anodization processes	Ion nitroding; ion carburizing; plasma oxidation
	Disproportionation processes	Deposition of molecular species; formed in gas phase
Conversion processes	Thermal diffusion	Diffusion of material from surface into bulk of substrate
Etching processes	Chemical etching	Acidic solutions; lye etching
	Ion etching	Sputter process
Mechanical processes	Grinding; peening; polishing	

The characteristics, properties, and tribological performance of coatings and modified surfaces can be strongly influenced by the process used. For example, it has been found difficult to produce with the plasma arc spraying process thin ceramic coatings (thickness of the order of a micrometer or less) for precision parts with small tolerances, which have a coating thickness uniformity of 1 percent or better, with accurate stoichiometry over a large coating volume, and with high density (approaching theoretical density). Such difficulties have been reduced or eliminated through the use of other processes, such as certain plasma-assisted physical vapor deposition processes—e.g., a high-rate reactive sputtering process patented by Borg-Warner (Sproul, n.d.) or an activated reactive evaporation process patented by Bunshah of UCLA (Bunshah, 1981). Plasma-sprayed coatings, however, have also found wide use in different industrial applications— e.g., as thick thermal barrier coatings, with thicknesses exceeding several millimeters, or as thick ceramic coatings of gas turbine blades and vanes for increased corrosion resistance. More details about major advantages and disadvantages of various coating and surface-modification processes are given by Bunshah, 1983; Lowenheim, 1977; Dearnaly et al., 1974; Williams and Poate, 1984; and Picraux and Choyke, 1982.

RECOMMENDATIONS

Ceramic Fabrication

Tribological studies of ceramics must consider the variables that might arise due to the fabrication process and incorporate these into the evaluation procedure for the tribological study. As a minimum, the ceramic should be well characterized prior to the tribological study. Specifically, this should include bulk chemistry, microstructure, surface structure (asperities, residual stress, cracks, etc.), pore distribution, strength, elastic modulus, Poisson's ratio, and fracture toughness.

Research is needed to acquire more understanding of the relationships among process parameters (and the resulting structure), physical and mechanical properties, and the resulting tribological performance. This not only would permit the optimization of a given process, but also would provide a basis for selecting from alternate fabrication techniques.

REFERENCES

Bunshah, R. F. 1981. The Activated Reactive Evaporation Process: Developments and Applications. Thin Solid Films, Vol. 80, Nos. 1, 2, and 3, pp. 255-261.

Bunshah, R. F. 1983. Deposition Technologies for Films and Coatings--Development and Applications. Park Ridge, New Jersey: Noyes Publication.

Dearnaly, G., J. H. Freeman, R. S. Nelson, and J. H. Stephen. 1974. Ion Implantation. In Defects in Crystalline Solids Series, Vol. 8. Amsterdam: North-Holland Publishing Group.

Lowenheim, F. A. 1977. Electroplating: Fundamentals of Surface Finishing. New York: McGraw-Hill.

Mangels, J. A., and G. L. Messing (eds.). 1984. Advances in Ceramics, Vol. 9, Forming of Ceramics. Columbus, Ohio: American Ceramic Society.

Onoda, G. Y., Jr., and L. L. Hench (eds.). 1978. Ceramic Processing Before Firing. New York: John Wiley and Sons, Inc.

Picraux, S., T. Thomas, and W. J. Choyke (eds.). 1982. Metastable Materials Formation by Ion Implantation. Amsterdam: North-Holland Publishing Group.

Richerson, D. W. 1982. Modern Ceramic Engineering. Properties, Processing and Use in Design, Chapter 6. New York: Marcel Dekker, Inc.

Sproul, W. n.d. Borg-Warner, U.S. Patent 4,428,811.

Wang, F. F. Y. (ed.). 1976. Treatise on Materials Science and Technology, Vol. 9, Ceramic Fabrication Processes. New York: Academic Press, Inc.

Williams, J. S., and J. M. Poate (eds.). 1984. Ion Implantation and Beam Processing. New York: Academic Press.

Chapter 4

INFLUENCE OF LUBRICATION ON BEHAVIOR OF CERAMIC TRIBO-ELEMENTS

Effective control of friction, wear, and fracture of ceramic-metal and ceramic-ceramic contact interfaces through lubrication is crucial to the success of many advanced technologies. Ceramics are inorganic materials usually formed under high-temperature sintering; they possess many unique properties such as high strength, high hardness, dimensional stability, corrosion resistance, and stability. The advanced ceramics, with their finely controlled microstructures and chemistry, have given rise to new opportunities for technologies such as heat engines, sophisticated electrical controls, electronic substrates, microwave guides, wear parts, cutting tools, fiber optics, and optical thin films. Ceramics, being highly refractory, are relatively brittle and fracture easily, causing catastrophic failures. A knowledge of lubrication of this class of materials is therefore essential for their effective application.

Proper lubrication can dominate many of the other factors. It can substantially reduce the coefficient of friction and thus minimize surface stresses. It can reduce frictional heating and keep the interface below temperatures where detrimental chemical reactions can occur. It can also act as a surface boundary layer to keep chemically active gases, liquids, and solids away from the ceramic surface.

There are many research issues in lubrication of ceramics. Because of the wide temperature range over which the materials can be used, research needs perhaps are best described under the categories of low temperatures (room temperature to 200°C), intermediate temperatures (200 to 600°C), and high temperatures (600 to 1500°C). Research issues in different temperature ranges often change as the environment and materials change with the temperatures, and they also vary with different classes of lubricants: gases, liquids, solids, and coatings.

TEMPERATURE REGIMES (<200°C)

In the temperature range of ambient to 200°C, many components and systems today operate with liquid lubricants. Specialty solid lubricants such as

29

graphite or molybdenum disulfide also are used. Application knowledge of these lubricants with metal systems are reasonably well understood. Many studies are being conducted on lubrication mechanisms of additives on metals. However, very few studies have been or are being conducted on the lubrication requirements of ceramics.

Ceramic tribo-elements usually are given a smooth surface texture, due in part to the need to remove microcracks from the surface. Hence, they are well suited for hydrodynamic (fluid film) lubrication. Under boundary lubrication conditions, ceramics, because of their relatively low thermal diffusivity, would tend to have much higher surface temperatures and resulting high interface temperatures.

Most liquid lubricants consist of base oils and additives. The antiwear additives frequently are developed on the basis of the chemical reactivity of the additive with iron. Because ceramics contain many different elements, such as silicon, zirconium, aluminum, and boron in the forms of oxides, nitrides, and carbides, the reactivity of additives with these elements under tribochemical conditions is not yet defined. Unlike metals, where current technologies are largely defined by iron-based alloys, these elements may have entirely different chemistry with hydrocarbons and additives. Element-specific lubrication chemistry may be required for effective friction and wear control.

Many value-added components that pervade industry, such as pumps, valves, tools, bearings, and gears, could use advanced ceramics to improve performance and durability. Lack of effective lubrication knowledge will impede further use of ceramics for these value-added components.

TEMPERATURE REGIMES (200 to 600°C)

The temperature range of 200 to 600°C has been and currently is very important for ceramic applications. Technologies embraced in this temperature range are high-temperature bearings, cutting tools, materials processing systems, and advanced combustion systems. Although lubricants in this temperature range have been intensively studied (Sliney and Johnson, 1968; Sliney, 1982; Sharma et al., 1983; Longson, 1983; Cosgrove et al., 1959; Christy, 1982), a systematic data base has not been developed. In practice, a wide variety of lubricants have been used with a relatively small number of ceramic materials. Hot-pressed silicon nitride is the most used ceramic material in various lubricant testing programs. Silicon carbide, zirconia, and reinforced alumina have also been evaluated. Titanium carbides and nitrides have been used for coatings, as have chromium oxides. Lubrication in the intermediate temperature range is complicated, not only in the wide variety of applications and the different environmental factors involved, but also in the lubricant delivery system, system compatibility, lubricant degradation, materials changes, lubricant-material reactivity, and diffusion. All these factors have a significant impact on system durability.

TEMPERATURE REGIMES (>600°C)

When the temperature goes above 600°C, very few conventional lubricants will function. The choice appears to be between high-temperature oxides, fluorides, mixed oxides, glasses, silver, gold, solid composites, and vapor-phase coating of chemically active species for short-period lubrication.

At high temperatures, coke and residue formation may be deleterious to some rubbing systems. Reactivity with the substrate needs to be balanced with corrosiveness. Because of the higher chemical reaction rates, active species may react and desorb rapidly, forming a corrosion product. Degradation of lubricant molecules and the formation of corrosive species is another serious consideration. However, this technology appears to hold promise for an easy and economical way to lubricate ceramic materials at temperatures above 600°C and should be pursued.

Solid lubricants at high temperatures in the form of oxides, fluorides, glasses, mixed oxides, graphite, and dichalcogenides of tungsten, molybdenum, niobium, and tantalum can be used. Lubricants are applied in many forms; these are discussed in later sections of this chapter.

At high temperatures, chemical reactivity between the lubricant and ceramic substrate is important. Calcium fluoride, barium fluoride, and lithium fluoride have high reactivity with many ceramic materials, such as alumina, zirconia, and silicon nitrides. New structures may form at the surface, resulting in either beneficial or deleterious effects on friction and wear. Thermodynamic data at high temperatures and phase equilibria and high-temperature solubilities of mixed oxides and fluorides are currently not available. Thermodynamic models for predicting these relationships need to be developed.

The natural tendency for materials to adhere under sliding conditions increases with temperatures. Successful lubrication of ceramic surfaces above 600°C must take into account the lubricant and substrate stability as a function of time. At high bulk temperatures and even much higher surface temperatures, the lubricant will undergo degradation and change. Diffusion within the substrate will increase with the temperature, causing surface segregation. Lattice vibrations will increase in amplitude, enhancing plastic deformation and dislocation mobility. When the temperature approaches half the melting point, deformation by creep becomes the dominant mechanism of the material under shear stresses. The lubricant has to maintain adhesive bonds with the changing substrate.

Lubricant resupply and disposal of degraded lubricant at high temperatures is an application concern. Disposal of wear debris from the surfaces could become a problem, resulting in abrasive wear. Degraded lubricant could form deposits on the surfaces, creating barriers to new lubricant supply.

Very few lubricants have been demonstrated to be effective and durable at temperatures above 600°C. Even fewer have been tested on ceramic surfaces.

There is a need both to understand lubrication mechanisms and to find new lubricants for high-temperature applications.

LUBRICANT TYPES

Gases

Both inert gases and air have been used to provide fluid film support for bearings and other tribological contacts. Because of the limited load capacity and restrictions in terms of gas supply and bearing design, very few industrial systems use gas lubrication. Because no surface contact takes place under the air or gas bearing concept, the choice of the surface material is not as significant as in other cases. The key issue in this area has been the difficulty encountered during start-up and variable-speed operations, under which wear and adhesion become a problem.

Vapor-phase lubrication, via surface chemical reactions to form a strongly adhered protective film on the surfaces, is an attractive alternative (Pinto et al., 1984; Butler and Popovic, 1974; Buckley and Johnson, 1959). The concept is to deliver vapor-phase-reactive compounds at high temperatures to the rubbing contacts. The subsequent reaction film, if tenacious, will protect the surfaces for a short time against high shear stresses. Phosphate esters and melissic acid have been found to be useful for steel surfaces at temperatures up to 700°C. Liquid phosphate esters have also been used with a ceramic engine prototype and were found partially satisfactory. Klaus and coworkers (1986) have demonstrated that phosphate esters deposited between 300 and 900°C on steel surfaces are capable of forming a tenacious film with thickness on the order of 1000 molecular layers. The deposition rate and reaction rates are dependent on oxygen partial pressure, temperatures, and substrate materials. It has been demonstrated that a low concentration of 0.2 percent by weight of tributyl phosphate (TBP), tricresyl phosphate (TCP), and diphenyl-di-tert-butylphenyl phosphate (DPTBPP) in the vapor stream is sufficient to protect the steel surfaces at 371°C.

The attractiveness of the vapor-phase lubrication concept lies in the simplicity and ease of lubricant delivery. A minute amount of lubricant can be metered out over a period of time to protect the wearing surfaces. In the heat engine case, the lubricant may be added in the fuel and deposited directly on the cylinder liner during combustion.

Research issues in this area are the lack of basic understanding of the chemical reaction mechanisms, the nature of the reaction products, and the reactivity with various ceramic substrates.

Liquids

The use of liquid lubricants in heat engines in the temperature range of 200 to 600°C is limited. At the same time, liquid lubricants are desirable to flush the system, to start the engine at low temperatures, and to remove wear debris. For heat engines, even though the temperatures at the piston ring and cylinder liner will approach 400 to 600°C in the near term, the engine sump temperature may only be 150 to 200°C. Very few liquid

lubricants can operate above 300°C for any substantial length of time. However, there are two possible concepts: controlled burning of lubricants and a combination of liquid-solid lubrication. In the latter case, the liquid lubricant will operate under a certain temperature range. When a preset temperature is reached, the liquid lubricant flow is shut off and the solid lubricants begin to function. A very stable liquid lubricant therefore is needed.

There is extensive literature as well as a significant amount of industrial experience on metal lubrication via additives in liquid base oils. For ceramics, however, very few studies have been conducted. Shimauchi and coworkers (1984) conducted both laboratory and prototype single-cylinder engine endurance tests to assess the effects of liquid lubricants on ceramic components. They concluded that different liquid lubricants affected the performance of various ceramic surfaces significantly. The tests were conducted using different liquid lubricants on various material pairs under controlled laboratory tribological testing. The materials consisted of various plasma-sprayed coatings 0.2 mm thick (including chromium oxides, carbides, titanium and tungsten carbides, zirconia, and chromium oxide with vanadium carbides). Only one oil, an ester fluid without additives, functioned reasonably well.

Data from Garrett's turbo-compound engine program also show that the choice of liquid lubricant is of paramount importance (Keiser and Castor, 1981). That program tested an extensive list of materials and lubricants at 650°C. Again, esters appeared to be a promising candidate to control friction and wear of various superalloys, ceramics, and composites. An extensive data base like this yields valuable information through trial and error, but little fundamental understanding is gained. Why a particular ester family functioned well and other esters would not function under the same conditions was not clear. Fundamental studies will yield a knowledge base from which future lubricants and additives for ceramics may be developed.

The key issue in the area of liquid lubricants for heat engines is the basic understanding of surface chemical reactions between the liquid lubricants and the ceramic surfaces. For silicon carbides and nitrides, a limited data base of silicon chemistry exists in the geochemistry and semiconductor areas. For example, water reacts rapidly with silicon through hydrolysis reactions and forms various hydrides with different friction and wear characteristics. In fact, the reactivity of water with many ceramic materials has long been recognized and utilized in ceramic machining. Zirconia, on the other hand, may not respond to water or other silicon-specific chemistry. In metal systems, controlled chemical reaction rates have proved to be a key for effective lubrication. No corresponding data base exists for ceramics.

The availability of additives and the understanding of additive mechanisms at high temperatures is critical (Fehrenbacher, 1985). Oil evaporation, degradation, degradation products, degradation product corrosiveness with materials, and the effective control of emissions are other significant technical challenges in this area. A detailed discussion of some aspects of this subject has been presented by Fehrenbacher (1985).

Lubricants also exist in a liquid state at high temperatures (above 600°C). However, most of these lubricants are solids at room temperature. Thus, before a device lubricated by high-temperature lubricants such as silicates and borates can be utilized, the sliding surface must first be heated. This limits their potential applications.

Solids

One interesting aspect of ceramic lubrication is that, to date, very few studies have been conducted using solid lubricants on ceramic surfaces. The majority of the studies of ceramic materials in the form of either coatings or solid materials are tested at room temperature or moderate temperatures (300°C) with a liquid lubricant. Several studies of ceramic materials have been reported (Shimauchi et al., 1984; Keiser and Castor, 1981).

There are many studies related to the use of solid lubricants for metals under severe environments (American Society of Lubrication Engineers, 1971, 1978, and 1984; Weilbach, 1982). A number of reports (Gardos, 1982; Yonushonis, 1980 and 1983; Ling, 1985; Lucek, 1979; Dayton and Sheets, 1976; Fusaro, 1982 and 1983) specifically examine solid lubricants for ceramics. Solid lubricants used in these studies are varied but mainly consist of layer lattice solids (graphites, molybdenum disulfides, graphite fluorides, tungsten sulfides, etc.), polyimides, oxides, and polytetrafluorethylene (PTFE). In this section, the discussion is limited to the temperature range of 200 to 600°C.

While there are many solid lubricants, the choice of solid lubricant delivery method is critical to successful application. Solid lubricants can be supplied through transfer films, coatings, liquid suspension, gas suspension, bonded films, powder compact, surface modification, or burnished coatings. In many of these methods, lubricant-substrate bonding, adhesion, and reactivity are crucial to the success of lubricant delivery. Again, experience with these methods and materials combinations is mostly with metal systems. Very few ceramic substrates have been studied. Based on metal system experience, the critical issues are lubricant-substrate or lubricant-surface adhesion; lubricant-surface reactivity and bonding strength; rate of adhesion and reaction; and lubricant film stability, strength, and durability.

The effectiveness of the lubrication obviously depends on how readily and how strongly the solid lubricant adheres to the surface or substrate. In the case of solid lubricants carried by gas, the lubricant has a relatively short period of time to adhere to the surface. Once at the surface, the bonding strength of the solid film with the substrate is important. Often this is achieved through the chemical reaction between the solid lubricant and the surface or substrate materials. In ceramics, the adhesion and reaction may be a problem with many solid lubricants. The high-temperature kinetics of solid lubricants with ceramic surfaces have simply not been tested. In many cases, depending on the method of delivery, the relative rates of adhesion and reaction with the amount of time allowed by the rubbing action may be important. At high temperatures, desorption or other unfavorable reactions such as phase change or new compound formation may also interfere with the normal processes of lubrication.

Surface-connected porosity has potential to be beneficial in the case of lubrication, especially solid lubrication. The porosity can aid in lubricant adhesion to the ceramic and might even provide a reservoir for replenishment.

Because of the wide variety of materials and potential solid lubricants, and also the additional variation introduced by the methods of lubricant delivery, a systematic assessment of lubricant-ceramic combinations is needed. Table 4-1 lists some commercially available solid lubricants and their temperature limitations with metal systems. Notice that most solid lubricants in air have a maximum operating temperature in the range of 200 to 500°C. These are, however, adequate for some heat engine applications. Table 4-2 lists the estimated life of some of the solid lubricants in the piston ring zone at projected heat engine conditions and temperatures.

The basic mechanisms of how solid lubricants work even at low to moderate temperatures are not well understood. Graphite and MoS_2 have been studied extensively. Other higher temperature materials have not been systematically investigated. At high temperatures (600°C), reactivity of the lubricant with the substrate and the degradation of the lubricant either through oxidation and/or thermal degradation complicate the mechanistic understanding. Under tribochemical conditions, where enhanced reaction rates arise because of bond rupturing and the presence of the dangling bonds, many reactions occur that normally would not take place. These areas of surface adhesion and chemical reactivity are largely untouched in metal systems.

Testing of ceramic materials at high temperatures (650°C) has been very limited (Longson, 1983; Weilbach, 1982; Gardos, 1982; Yonushonis, 1980 and 1983). Lubricants used include cesium molybdate complex, gallium-indium-tungsten diselenide ($Ga/In/WSe_2$) compact, tungsten disulfide, polyimide, metal-free phthalocyanine, graphite, and calcium fluoride-barium fluoride eutectic in nickel foam. Ceramic materials used were primarily silicon nitrides and silicon carbides. Most of the test results reported poor performance compared to conventional metal systems under approximately the same speed and load conditions. The ceramic counterpart at high temperatures typically lasted 1 or 2 hours, compared with thousands of hours of operating time for metals.

One of the technical challenges mentioned by many researchers involved in ceramic bearing testing with solid lubricants is the rapid rise in temperatures at the interface. Ceramics have lower thermal diffusivity than metals. Ceramics, being brittle, fracture relatively easily, producing high friction under boundary lubrication conditions. Frictional heating can produce extremely high flash temperatures and interfacial temperatures. If one goes to higher temperature lubricants such as oxides (bonded $PbO-SiO_2$) or inorganic salts, the friction often is quite high (coefficient of friction 0.2 to 0.8). Many high-temperature solid lubricants such as glasses and fluorides are brittle and abrasive below their softening-point temperatures. Thus, a combination low-temperature lubricant and high-temperature lubricant will be necessary.

TABLE 4-1 Commercial Solid Lubricants

Material	Acceptable Usage Temperature, °C				Average friction Coefficient		Remarks
	Minimum		Maximum				
	In Air	In N$_2$ or Vacuum	In Air	In N$_2$ or Vacuum	In Air	In N$_2$ or Vacuum	
Molybdenum disulfide, MoS$_2$	-240	-240	370	820	0.10-0.25	0.05-0.10	Low f, carries high load, good overall lubricant, can promote metal corrosion.
Polytetrafluoroethylene (PTFE)	-70	-70	290	290	0.02-0.15	0.02-0.15	Lowest f of solid lubricants, load capacity moderate and decreases at elevated temperature.
Fluoroethylene-propylene copolymer	-70	-70	200	200	0.02-0.15	0.02	Low f, lower load capacity than PTFE.
Graphite	-240		540	Unstable in vac.	0.10-0.30	0.02-0.45	Low f and high load capacity in air, high f and wear in vacuum, conducts electricity.
Niobium diselenide, NbSe$_2$			370	1320	0.12-0.40	0.07	Low f, high load capacity, conducts electricity (in air or vacuum).
Tungsten disulfide, WS$_2$	-240	-240	430	820	0.10-0.20		f not as low as MoS$_2$, temperature capability in air a little higher
Tungsten diselenide, WSe$_2$			370	1320			Same as for WS$_2$
Lead sulfide, PbS			480		0.10-0.30		Very high load capacity, used primarily as additive with other solid lubricants.
Lead oxide, PbO			650		0.10-0.30		Same as for PbS.
Calcium fluoride-barium fluoride eutectic, CaF$_2$-BaF$_2$	430	430	820	820	0.10-0.25 above 540°C 0.25-0.40 below 540°C	Same as in air	Can be used at higher temperature than other solid lubricants, high f below 540°C.
Antimony trioxide, Sb$_2$O$_3$							High load capacity, used as corrosion inhibitor in MoS$_2$ lubricants.

Source: Kirk-Othmer "Encyclopedia of Chemical Technology," 3rd Edition.

TABLE 4-2 Estimated Life of Solid-Lubricated Piston Rings

Material	Best K[a]	T_{max} (°F)	Estimated Life[b] (hours)
Unlubricated ceramic	12×10^{-8}	1800	12
Plug-lubricated ceramic	1.2×10^{-8}	1000	120
Bonded film	3×10^{-8}	700	0.4
Carbon graphite	2×10^{-8}	1000	100
Filled Teflon	6×10^{-8}	500	17
Polyimide	18×10^{-8}	800	14
NASA hi-temp film	30×10^{-8}	1600	2.3
Metal matrix composite	100×10^{-8}	1000	1.7

Source: Owens, 1985

[a]Dimensionless wear coefficient, $K = \frac{HV}{DL}$ (H = hardness, V = wear volume, D = distance traveled, L = load)
[b]Life based on 0.020 in. wear under typical conditions, P = 300 psi

RECOMMENDATIONS

In the area of ceramic lubrication, the most urgent need is to develop an effective lubrication system so that ceramics can be utilized effectively. To accomplish this, research in several areas needs to be addressed:

Lubrication Mechanisms

■ Low temperature (bulk temperature) applications are going to create the largest short-term markets for structural ceramics. The chemical reactivity between hydrocarbon structures with ceramic surfaces needs to be defined. The mechanisms of reaction and rates of reaction under boundary lubrication conditions should be studied to examine the structural effects, functional group influence, and the physical properties effects.

■ Surface forces at ceramic surfaces need to be measured. The additional double layer forces at ceramic surfaces will effect adsorption, lubricant-substrate adhesion, wetting, and reactivity.

■ Lubrication mechanisms of solid lubricants at high temperatures need elucidation. Effects of diffusion, segregation, reactions, degradation on adhesion, and surface protection need careful study. The formation of new phases, reaction products at high temperatures, with and without tribocontacts, needs to be defined.

• Thermodynamic equilibrium of phases and solubilities of the lubricant and substrate needs to be experimentally determined and subsequently predicted by models.

• Degradation mechanisms of lubricants and their influence on friction and wear over the temperature ranges should be studied.

Lubricant Development

• Element-specific chemistry based additives that provide friction and wear control through the formation of protective friction and wear control through the formation of protective films need to be developed.

• High temperature antioxidants that can survive 400°C for a short period of time should be developed. Various mechanisms may be operative in this temperature.

• For heat engine applications, high temperature (400°C) ashless dispersants and acid neutralizers are needed.

• Novel compositions in synthesizing high temperature liquid lubricant need to be explored.

Lubricant Delivery and Disposal Research

• Vapor phase-deposited lubricants for short duration protection constitute a very attractive concept. Functionality, reactivity, deposit control, and reaction mechanisms need to be systematically investigated.

• Impregnation of lubricants into the materials substrate by coatings, physical vapor deposition, ion beam mixing, and self-lubricating composites should be explored.

• Spent lubricant and wear debris will be deleterious to system durability. Mechanical design changes as well as chemical means in removing them may be critical to the lubricant selection.

In ceramic lubrication research fundamental information is lacking. While the technology of metal lubrication has matured, detailed mechanisms are not fully understood. Thus information transfer from existing technologies to ceramic lubrication may be very few. A systematic effort is defining the surface energy, surface reactivity, surface composition of simple single crystals with different molecules under different environmental factors needs to be established.

REFERENCES

American Society of Lubrication Engineers. 1971. Proceedings of the International Conference on Solid Lubrication, Denver, Colorado, August 24-27.

American Society of Lubrication Engineers. 1978. Proceedings of the 2nd International Conference on Solid Lubrication, Denver, Colorado, August 7-10.

American Society of Lubrication Engineers. 1984. Proceedings of the 3rd International Conference on Solid Lubrication, Denver, Colorado, August 7-10.

Buckley, D. H., and R. H. Johnson. 1959. Halogenated gases for high temperature lubrication of metals. Ind. Eng. Chem., Vol. 51, No. 5, p. 699.

Butler, A., and N. Popovic. 1974. Vapor deposition of lubricant. Lubr. Eng., Vol. 30, No. 2, pp. 59-61.

Christy, R. I. 1982. Lubrication for Rolling Element Spacecraft Parts. Tribology International (October).

Cosgrove, S. L., L. B. Sibley, and C. M. Allen. 1959. Evaluation of dry powdered lubricants at 1000°F in a modified four-ball wear machine. ASLE Trans., Vol. 2, No. 2, pp. 217-223.

Dayton, R. D. and M. A. Sheets. 1976. Evaluation of Grooved Solid Lubricated Bearings. AFWAL-TR-75-76 (February).

Fehrenbacher, L. 1985. Identification of Tribological Research and Development Needs for Lubrication of Advanced Heat Engines. Final Report, ORNL Contract 86X-47986V (April). Oak Ridge, Tennessee: Oak Ridge National Laboratory.

Fusaro, R. L. 1982. Polyimides: Tribological Properties and Their Use as Lubricants. NASA-TM-82959. Washington, D.C.: National Aeronautics and Space Administration.

Fusaro, R. L. 1983. Polyimides Formulated From a Partially Fluorinated Diamine for Aerospace Tribological Applications. NASA-TM-83339. Washington, D.C.: National Aeronautics and Space Administration.

Gardos, M. N. 1982. Solid Lubricated Rolling Element Bearings. Hughes Report No. FR 83-76-663 (October).

Keiser, R. J., and J. G. Castor. 1981. Compound Cycle Turbofan Engine Materials Report. AFWAL-TR-81-2141, DARPA Contract F33657-77-C-0391 (final report).

Klaus, E. E. et. al. 1986. Vapor Phase Lubrication. DOE ECUT Tribology Progress Reports, 1983-1986. Washington, D.C.: U.S. Department of Energy.

Ling, F. F. 1985. Fundamentals of High Temperature Friction and Wear With Emphasis on Solid Lubrication for Heat Engines. U.S. Army, ARO Contract DAAG 39-84-M-0479 (June).

Longson, B. 1983. Lubrication of High Temperature Ceramic Materials. Tribology International, Vol. 16, No. 4, p. 221.

Lucek, J. W., L. B. Sibley, and J. W. Rosenlieb. 1979. Severe Environment Testing of Silicon Nitride Rolling Elements. NAVAIR Contract N00019-77-C-0551 (March).

Owens, E. 1985. In Fundamentals of High-Temperature Fiction and Wear With Emphasis on Solid Lubrication for Heat Engines. F. F. Ling (ed.). U.S. Army Contract DAAG39-84-M-0479 (June).

Pinto, N., J. L. Duda, E. E. Graham, and E. E. Klaus. 1984. In Situ Formation of Solid Lubricating Films From Conventional Mineral Oil and Ester Base Lubricants. Proc. 3rd Inter. Conf. on Solid Lubr. American Society of Lubrication Engineers.

Sharma, S. K., P. Vasudevan, and U. S. Tewari. 1983. High Temperature Lubricants: Oils and Greases. Tribol. Inter., Vol. 16, No. 4, p. 213.

Shimauchi, T., T. Murakami, T. Nakagaki, A. Y. Tsuy, and K. Umeda. 1984. Tribology at High Temperature for Uncooled Heat Insulated Engine. SAE Paper 840429. Warrendale, Pennsylvania: Society of Automotive Engineers.

Sliney, H. E., and R. L. Johnson. 1968. Preliminary evaluation of greases to 600°F and solid lubricants to 1500°F in ball bearings. ASLE Trans., Vol. 11, pp. 330-337.

Sliney, H. E. 1982. Solid lubricate materials for high temperatures--a review. Tribol. Inter. (October).

Weilbach, A. O. 1982. High Temperature Bearing and Dry-lubricated Concepts, Phase I. Final Report, DARPA/ONR Contract N00014-82-C-0248. Rancho Cucamonga, California: Mindrum Precision Products.

Yonushonis, T. M. 1980. Dry Lubrication of High Temperature Silicon Nitride Rolling. Contract NAVAIR N00019-79-C-0612, Final Report. Avon. Connecticut: SKF Company.

Yonushonis, T. M. 1983. Solid Lubricated Silicon Nitride Bearings at High Speed and Temperature, Phase II. Contract NAVAIR N00019-81-C-0473. Avon, Connecticut: SKF Company.

SUGGESTED ADDITIONAL READING

Horton, P. H., and W. J. Kurzeka. 1969. Development of Nuclear Reactor Bearings for 1500°F Space Operation. ASME Paper 69-WA/Lub-11. New York: American Society of Mechanical Engineers.

Matt, R. J., et al. 1963. Research and Development of Airframe Bearings for Aerospace Vehicles. Technical Documentary Report ASD-TRD-63-716 (September).

Rabinowicz, E., and M. Imai. 1961. Friction and Wear at Elevated Temperatures. Report WADC-TR-59-603, Part 2 (May). Wright-Patterson Air Force Base: Wright Air Development Center.

Riesz, C. H., and H. S. Weber. 1962. Mechanism of Wear of Nonmetallic Materials. Report WADC-TR-59-316, Part 4 (June). Wright-Patterson Air Force Base: Wright Air Development Center.

Sliney, H. E. 1960. Lubricating Properties of Some Bonded Fluoride and Oxide Coatings for Temperatures to 1500°F. Report NASA TN D478 (October). Washington, D.C.: National Aeronautics and Space Administration.

Taylor, K. M., et al. 1961. Development of a Ceramic Rolling Contact Bearing for High Temperature Use. ASME Paper Gl-Lub-12. New York: American Society of Mechanical Engineers.

Zeman, K. P., W. R. Young, and L. F. Coffing. 1959. Friction and Wear of Refractory Compounds. Report APEX 625 (May). Schenectady, New York: General Electric Company.

Chapter 5

STRUCTURE, COMPOSITION, AND REACTIVITY OF CERAMIC SURFACES

The friction and wear of ceramics and their reaction to lubricants depend in a great measure on their surface properties (Buckley, 1972; Buckley and Miyoshi, 1985). It is well known that most properties of a solid are often different on the surface from what they are in the bulk and are determined by a dynamic interaction of the solid with its environment. The surface topography, for instance, affects whether a machine operates in the hydrodynamic, mixed, or boundary lubrication regime. With metal machinery, this surface topography is usually modified in early stages by the process of break-in, in which plastic deformation and wear of the surfaces brings about a more ideal mating of the two sliding bodies and improves lubrication. With ceramics, which usually wear by fracture rather than plastic deformation, this break-in period may produce a rougher rather than a smoother surface and can degrade the machine rather than improve it. The break-in will depend on the surface hardness of ceramics or their plasticity; there have been many investigations that show that the surface of a ceramic is rendered more plastic by the environment (the Rehbinder effect) or, in other situations, that the environment will embrittle the material and accelerate crack propagation. In a similar vein, the surface composition of the ceramic, which is determined by chemical interaction of the material with the environment, will influence the adhesion between the ceramic and the counterface, and therefore the friction coefficient. Recent work has shown that friction causes a large increase in the reactivity of ceramics over what it is in the absence of friction. This tribochemistry can be beneficial, since the reaction can produce soft surface layers that distribute the stresses and decrease the mechanical forms of wear. It is therefore obvious that knowledge of the surface properties of ceramics can greatly assist further progress in their application in tribological situations. The surfaces of interest will include the one or two uppermost layers of atoms that control adhesion, adsorption, and lubrication phenomena as well as a more extended "near-surface" layer that determines the mechanical behavior of the material and its wear resistance. The depth of this near-surface layer extends as far as its properties are different from those of the bulk. What follows is an attempt to summarize the state of knowledge of the surface properties of these materials.

SURFACE STRUCTURE

The ceramic materials of tribological interest are either single crystals, used mostly in fundamental studies, or polycrystalline materials, which are used in the vast majority of practical applications. When we consider the surface structure of ceramics, we must include the arrangement of atoms on the surface of single crystals, the geometry and orientation of the crystallites in a polycrystalline material, and the modifications brought about in both of them by the action of friction and wear.

Most solids in which the chemical bonding is strongly influenced by geometry of the atomic orbitals (such as the covalent solids, Si and Ge, and the transition metals with a large fraction of d-electron contribution to bonding such as Pt, Ir, and Au) possess an arrangement of the atoms at their surface that is different from their bulk positions in such a way as to minimize the surface energy. These reconstructed surfaces are chemically less active than unreconstructed ones, but environments that react strongly with the solid create their own surface structure. We expect that the covalently bonded ceramics will also display a reconstructed surface structure. To date, only silicon carbide has been investigated. Natarajan and coworkers (1985) have applied an interesting novel technique (extended fine structure of electronic energy losses) with which they confirmed the known crystallographic structure of bulk silicon carbide. By using low-energy electron diffraction and Auger electron microscopy, Dayan (1985) has shown that the [100] surface of zinc-blended silicon carbide is indeed reconstructed and that the reconstruction is different on the carbon-rich and the silicon-rich surfaces. We have not been able to find any other investigations on the surface structure of ceramics. However, when we discuss the surface composition of ceramics, we shall see that adsorption of OH groups will probably modify the surface structure.

Metastable structures of certain ceramics (Kingery et al., 1976) such as ZrO_2 allow a martensitic transformation under stress, which confers a much-increased toughness to these materials. Since wear of ceramics occurs predominantly by fracture, increased toughness leads to increased wear resistance (Fischer et al., 1987). It has been reported (Hasesawa, 1983) that friction induces a transformation of the crystallographic structure in the near-surface layer of zirconium oxide to a rhombohedral phase that is not normally encountered in this material and increases its toughness. Many ceramics undergo tribochemical reactions during friction and acquire an amorphous surface layer (Fischer and Tomizawa, 1985). These amorphous layers exhibit different mechanical properties from the crystalline bulk and can, under the proper circumstances, decrease friction and wear.

Polycrystalline ceramics are produced by sintering, reaction bonding, or hot pressing. Usually, perfect density of these materials cannot be achieved, and voids exist between grains. These voids can act as stress concentrators and nucleation sites for surface cracks. Since ceramics are very brittle, the machining of these materials introduces microcracks and other defects in the surface that decrease their strength and their wear resistance. The relationship of microstructure, surface processing, and strength is being extensively studied for ceramics and is discussed in

Chapters 3 and 8. Miyoshi and Buckley (1982) and others before them have observed that friction and wear resistance of ceramics often show a strong dependence on the crystallographic orientation of the sliding surface.

BULK COMPOSITION

One of the reasons ceramics are considered for tribological elements is because the ceramics are chemically stable compared to metals. Metals in close contact have a strong tendency to adhere through the formation of chemical bonds. Rabinowicz (1984) reports a wear coefficient in the range of 10^{-3} for metals for severe galling due to adhesive wear. A comparable wear coefficient for adhesive wear of ceramics is 10^{-6}. The influence of chemical composition was discussed in Chapter 3.

The compositions of the powders used to fabricate a ceramic largely determine the chemical characteristics of the final dense ceramic as well as many of the physical and mechanical characteristics. The starting materials must be chemically analyzed to identify the level of impurities present. These impurities will generally remain in the ceramic throughout processing and will affect the tribology behavior. Major concerns are thermodynamic stability at the service conditions, avoidance of adhesion to the mating contact surface, and understanding of any potential chemical reactions that might occur at the contact interface (see Chapter 9). Knowledge of compatibility with an intended lubricant is also necessary for the complete range of application temperatures.

At the current state of technology, the composition usually cannot be selected to be optimum for all the tribology requirements. This is partly because we do not have an adequate data base to understand the complex interactions between composition and tribology. It is also partly caused by the composition compromises necessary to achieve densification or to control microstructure. Many ceramic powders will not densify to a strong, pore-free ceramic unless impurities (called sintering aids) are added. The sintering aids alter the surface tension of the ceramic particles at high temperature and allow material transport between adjacent particles so that the particles bond together and porosity is eliminated. The sintering aids may remain in the composition and modify the chemical activity of the ceramic relevant to tribological and mechanical behavior.

Substantial progress has occurred during the past decade in the development of high-purity reactive powders that can be densified with a minimum of sintering aid. This is likely to support development of stabler ceramics for tribological application. However, this also causes problems. There are now ceramics commercially or experimentally available that have a common generic name but vary broadly in chemical characteristics. For example, a wide range of Si_3N_4-based compositions exist, and all are marketed under the generic name of silicon nitride. The same is true for zirconia, alumina, and silicon carbide materials. This places a difficult burden on the tribology researcher in the screening and characterization of materials and emphasizes the need for standardization of test materials.

SURFACE COMPOSITION

In a series of investigations with silicon carbide single crystals, Miyoshi and Buckley (1982) demonstrated a direct relationship between surface composition of a ceramic and its friction coefficient. In varying the temperature of the material between room temperature and about 1500°C in an ultrahigh-vacuum system and measuring the friction coefficient as well as the surface composition by x-ray photoelectron (XPS) and Auger (AES) spectroscopy, they showed that at temperatures above 800°C the friction coefficient of SiC decreases precipitously because of surface segregation of graphite. Between room temperature and 400°C, these authors also measured a relatively low friction coefficient that they ascribe to surface carbon and oxygen contamination. In very early experiments, Bowden and Tabor (1964) had shown that the friction coefficient on diamond against itself is about 0.1 in room air but assumes very large values when measured in vacuum. They ascribed the low friction coefficient to water vapor that dwelt on the surface. These examples show that the surface of ceramics plays an important role in their tribological behavior.

Much work has been done on the surface composition of ceramics, especially SiO_2 and Al_2O_3, which are used in highly dispersed form as catalysts and as supports for metallic catalysts. The chemistry of silicon oxide surfaces is well described in a voluminous book by Iler (1979). In most cases the surface of silicon oxide is saturated with OH to which water molecules are attached by hydrogen bonds. The surface compositions of graphite, diamond, silica, titania, and alumina are described in a review article by Boehm (1966). Studies on dispersed ceramics have shown that hydration of oxides is a common phenomenon. Hydration of silica and alumina (Frisch, 1965) is irreversible at room temperature and can be reversed only at temperatures as high as 800°C. Hydration of TiO_2, by contrast, is reversible (Frisch, 1965). Hydrocarbons, especially the fatty acids, alcohols, and esters so important to boundary lubrication, are adsorbed on ceramics as well as they are on metal (Iler, 1979; Boehm, 1966). Pure paraffins such as hexadecane, which result in a high friction coefficient with metals, form boundary lubricants on ceramic surfaces (Si_3N_4 and ZrO_2) that generate friction coefficients as low as 0.1 (Jahanmir and Fischer, 1986). In this context it is well to remember that SiO_2 and Al_2O_3, and especially silica-alumina, contain strong acid and base sites that

are responsible for their catalytic action in cracking and isomerization of hydrocarbons (Fischer, 1974; Tanabe, 1970). The tribological importance of these acidic and basic properties lies in the fact that they have a great influence on the adhesive properties of these materials (Fowkes, 1982).

As the temperature increases, the chemical activity of the surface increases. Zirconium oxide (ZrO_2) and titanium oxide (TiO_2) become oxygen-deficient at the surface in a nonoxygen atmosphere at high temperature. Most metals plus most nonoxide ceramics form a surface oxide film when exposed to air on oxygen at elevated temperature. The surface oxide has different chemical characteristics and is generally softer than the base material. In some cases the oxide can provide lubrication; in others it leads to an increased rate of wear.

The degree of corrosion attack is largely controlled by the chemical aspects of the microstructure. Composition of both the grains and grain boundaries is important. If impurities are concentrated at grain boundaries, corrosion can preferentially attack the grain boundary phase and undercut the grains, resulting in material degradation to a greater depth than would normally occur with attack of the grains. Grain size and the relative ratio of grain volume to grain boundary area influence the rate of chemical interaction. Other microstructure features can also affect corrosion and other forms of chemical activity. Surface-connected porosity and surface cracks increase the surface area of material accessible to chemical attack and allow access to subsurface material.

For some materials the nature of the oxidation varies, depending on the partial pressure of oxygen. This is the case for silicon nitride and silicon carbide at elevated temperature. If the oxygen pressure is high enough, a coherent layer of SiO_2 will form on the surface and act as a diffusion barrier to further oxidation. The oxidation rate will be parabolic. If the partial pressure of oxygen is too low, a protective layer will not form. Instead, volatile SiO will form and the oxidation kinetics will be linear.

The tribological behavior of materials is often dominated by the thin surface layers that result from interaction of the material and the atmosphere. For instance, silicon nitride and silicon carbide interact with oxygen above about 800°C to produce a surface film of silicon dioxide. At higher temperatures the oxide layer forms more quickly and to a greater thickness. The silicon dioxide is amorphous initially and softens well below its melting temperature. This leads to surface sticking (usually above 1200°C) and a dramatic increase in the coefficient of friction (Smyth and Richerson, 1983). At a high enough temperature, the viscosity of the silicon dioxide decreases (Lindberg and Richerson, 1985). This behavior is illustrated for silicon carbide in Figure 5-1. It should be noted that the interior microstructure and composition of the silicon nitride or silicon carbide are not changed. The surfaces will be further altered in a vacuum. Oxide layers may volatilize, oxide ceramics may become nonstoichiometric at the surface, and some nonoxide ceramics may dissociate. This may increase the difficulty of achieving lubrication or a low coefficient of friction. In one silicon carbide material, friction and wear were reported to decrease under vacuum. Surface decomposition of the silicon carbide formed graphite that acted as a solid lubricant (Miyoshi and Buckley 1980).

Impurities, whether introduced from the atmosphere or from adjacent materials, can alter the chemistry at the surface. In some cases this results in a viscous surface layer that might impede relative motion and lead to a stress buildup. In other cases the impurities will lead to a corrosive surface composition. For example, impurities such as Na^+ and Ca^{2+} modify the SiO_2 layer on silicon nitride to yield a composition that can locally dissolve the silicon nitride to produce surface pits (Carruthers et al., 1983). These pits reduce the material strength and increase the coefficient of friction. A similar mechanism plagues metals in gas turbine applications, where sodium from sea water mist or road salt and sulfur from the fuel condense as Na_2SO_4 at temperatures in the range of 1200 to 1800°F and cause severe "hot corrosion."
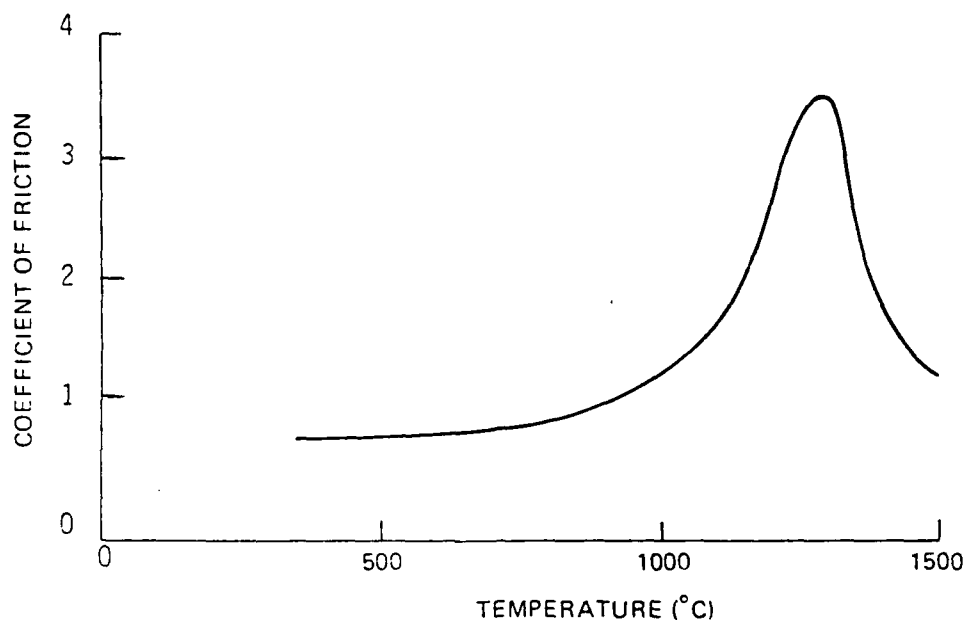
FIGURE 5-1 Coefficient of friction for SiC in air as a function of temperature (Lindberg and Richerson, 1985).

CHEMICAL REACTIONS

Ceramics have been selected for tribological use at high temperatures in part because of their chemical inertness. Recent investigations of friction and wear of ceramic materials in different environments have shown that friction, and especially wear, are strongly influenced by the chemical nature of the environments. This has already been shown in earlier work by Buckley (1972) and later by Shimura and Tsuya (1977) and by Wallbridge and coworkers (1983). Often the effect of the environment on wear has been interpreted in terms of the Rehbinder-Westwood (Westwood, 1974; Rehbinder, 1928) effect, which states that the hardness of the surface is modified by the environment. However, recent work by Fischer and Tomizawa (1985) has shown that friction vastly increases the rate of chemical reactions on the surface of ceramics, to the effect that the oxidation of silicon nitride occurs at the same rate at room temperature as it would without friction above 1000°C. These tribochemical reactions (Heinicke, 1984) have a profound effect on wear, an effect that can be beneficial since humidity in the atmosphere, for instance, decreases the wear rate of silicon nitride in unlubricated sliding by a factor of 100. At high temperatures, similar reactions can decrease the friction coefficient by forming a soft lubricating layer on the surface (Tomizawa and Fischer, 1986).

There is a large volume of literature dedicated to the surface chemistry of ceramic materials, mostly related to their application as catalysts, semiconductor passive layers, and refractories. Most theories of surface chemistry of ceramics are concerned with electron charge transfer and surface

acid-base properties. Much of the ceramic catalytic literature relates chemical activity to charge density and the probability for electron transfer at surface active sites (Knozinger and Ratnasamy, 1978; Campelo et al., 1984). Work in the field of adhesive bonding has also lead to the conclusion that electron transfer is responsible for adhesion of films to substrates (Deryagin et al., 1978) and to the hypothesis that blocking of charge transfer or reduction of electric fields would reverse reactions. Later work has demonstrated that total electron transfer is not required; intermediate hydrogen bonding reactions are also involved (Bolger and Michaels, 1968).

Alumina, magnesia, and silica are probably the most widely used ceramics. They possess similar electronic structures (Tossel, 1975; Ciraci and Batra, 1983; Ching, 1982), consisting of a split valence band of O 2s and O 2p orbitals with very little cationic characteristics. The conduction band is nearly entirely cationic 3s and 3p in nature and the band gaps are large, from 7.5 to 9.5 eV (Strehlow and Cook, 1973), making these oxides very hard acids and bases. The electronic structure of water is similar to that of these oxides (Franks, 1972). The oxides and water undergo typical acid-base reactions with charge transfer that causes dissociation of the water into protons and hydroxyls. Ions in solution are bonded to charged sites on the surface. All of these oxides have stable hydroxide surfaces and have pH-dependent solubilities in water that range from 10^{-3} for silica and 10^{-4} for alumina to complete dissolution for magnesia (Wiese, 1973). Dissolution in water is accelerated by friction enough to represent a measurable wear mechanism (Fischer and Tomizawa, 1985). Many complex ions adsorb into the surfaces of the oxides. Generally, these are the hard ions such as PO_4, SiO_4, and CrO_4, which form stronger electrostatic attractions than water and displace the latter from the surface. Others, such as SO_4 and NO_3 react more slowly (Katsanis and Matijevec, 1983). Organofunctional derivatives of these ions are also known to react with oxides; organosilianes and organophosphonic acids are used as coupling agents for paints and adhesives (Sung and Sung, 1981) and surface hydration inhibitors (Ahern et al., 1981). Reactions with organic compounds are limited to charge transfer reactions with highly polar functional groups such as alcohols, acids and amines, which dissociate or form polar hydrogen bonds (Iler, 1981; Bolger and Michaels, 1968). The oxide surfaces are known to catalyze ring opening reactions when the ring is small and highly polar (Pozner and Rogers, 1977). The tendency of alumino—silicates to catalyze alkene production, cracking, and isomerization is attributed to the electrophilic or nucleophilic reaction sites. With nonpolar organic species, no strong reactions are reported in the literature, though we have already mentioned the adsorption and boundary lubrication of paraffins during friction.

Silicon nitride and silicon carbide have narrow band gaps, 2.8 eV for SiC and 510 eV for Si_3N_4 (Strehlow and Cook, 1973). In addition, both materials have a strong tendency towards nonstoichiometry, which further reduces the band gap. One thus expects them to be soft acids and bases. Both materials react slowly with air or water to form the chemically more stable oxynitride or oxide surface coatings which have the chemical properties described above. At high temperatures they oxidize with a

parabolic rate (Babini et al., 1984; Kiehle et al., 1974; Dutta and Bazek, 1984) and the binder of the material influences the oxidation rate (Wu et al., 1981; Dutta and Bazek, 1984; Bouarroudj et al., 1985). The oxidation rate of silicon nitride in humid air is about 1000 times higher than it is in dry oxygen (Singhal, 1976), a behavior similar to that of metals. Because of oxidation, these materials have surface chemistries in air that are nearly identical to that of silica.

Zirconia possesses a band structure similar to that of the other oxides, but its band gap is only 5.0 eV (Strehlow and Cook, 1973). Because of this, zirconia is a softer acid-base than the other oxides or the oxidized surfaces

of SiC or Si_3N_4. Zirconia is, for instance, very weakly acidic in water (Ahmed, 1963; Ray, 1975). The reaction is a dissociation of the oxide to form Zr^{4+} and ZrO^2 in solution. As the concentration of the latter increases above 10^{-8}, complexation to $(Zr_4(OH)_8(H_2O)_{16})^{8+}$ and eventually recrystallization of the oxide occurs; no zirconium hydroxide is known to form (Regazzoni and coworkers, 1983). These weak interactions would seem to preclude the possibility of environmentally stimulated fracture that has been proposed to explain wear of ZrO_2 in humid environments (Fischer et al., 1987). It remains to be clarified whether the intergranular fracture observed in wear is due to interaction of water with zirconia, or with impurities, or the Y_2O_3 stabilizer, which has a slightly wider band gap (5.6 eV) and is much more reactive with water than ZrO_2 (Cotton and Wilkinson, 1980). The organometallic chemistry of zirconia is very rich (Cotton and Wilkinson, 1980). Zirconium compounds act as Ziegler-Natta catalysts for polymerization and cause hydrozirconation reactions which graft carbonyls onto alkenes to produce carboxylic acids. In tribological conditions, the potential exists for similar types of oxidation and catalysis reactions of organic lubricants with the surfaces or with wear debris to form complex oxidized oligomers.

HARDNESS AND STRENGTH OF CERAMIC SURFACES

The question of whether the hardness of solid surfaces is larger or smaller than that of the bulk is the subject of an old controversy for metals as well as ceramics (Latanision and Fourie, 1977). Of more importance to tribology is the question whether friction or tribochemistry produces a surface that is softer or harder than the bulk. It is, for instance, well known that dry sliding of steels in air produces a very hard martensitic layer on their surface. Westwood and his collaborators have studied the effect of the environment on the hardness of material (Westwood, 1974; Latanision and Fourie, 1977). They have found that it varies with the chemical composition of the environment and have established a correlation of the surface hardness with the zeta potential. (The zeta potential is the electric potential that exists in a thin liquid layer near the surface because of the adsorbed surface charges that are progressively screened by ions in the bulk of the liquid.)

Other researchers (Michalske and Bunker, 1984) are studying the environmentally stimulated fracture of ceramics. This effect is well known in glasses and in silicas where water vapor increases the propagation rate of

cracks. Michalske and Bunker established a model by which a water molecule attacks the silicon-oxygen bond by producing two SiOH sites on the surface. This reduction in cohesion facilitates crack propagation. On the other hand, Fischer and Tomizawa (1985) have shown that wear of silicon nitride in a humid ambient atmosphere produces a tribochemical reaction with accumulation on the surface of an amorphous sublayer that distributes the stresses and thereby decreases the mechanical wear by fracture. It is not yet known systematically under which conditions and for which ceramic materials ambient humidity increases wear by environmentally assisted fracture or decreases it by tribochemical formation of a soft surface layer.

RECOMMENDATIONS

Chemistry of Ceramic Surfaces

■ A systematic knowledge of the surface chemistry of ceramics (i.e., their surface composition, adsorption, surface reactions) must be acquired over a temperature range extending from 200 to approximately 1400°K. This is a prerequisite for the formulation of lubricants and additives.

■ The phenomenology and mechanism of tribochemistry of ceramics, defined as the chemical reactions induced or modified by friction, must be studied in the environment and in contact with the lubricants expected over the whole temperature range to be encountered in practice.

■ Surface characterization methods capable of detecting water and hydrogen must be further developed because of the widespread occurrence of surface hydration of ceramics.

■ Surface morphology and structure must be determined with very fine lateral resolution because of the importance of stress concentrations in the contact of hard bodies.

■ Surface crystallography must be studied as modified by friction. Toughening and embrittling phase transformations have been discovered and modify the friction behavior.

■ A better understanding of the hardness and toughness of ceramic surfaces must be obtained because of their influence on contact geometry and stresses.

■ The influence of adsorption on crack initiation and crack propagation plays an important role on wear and lubrication of ceramics. These phenomena demand an exhaustive experimental and theoretical study.

■ More progress must be made in the nondestructive detection of near surface flaws and cracks because the latter determine the reliability and wear resistance of ceramics and could vastly improve the manufacturing of these materials.

REFERENCES

Ahern, J. S., G. D. Davis, A. Desai, and J. D. Venables. 1981. U.S. Army Report AD-A206222.

Babini, G. N., A. Bellosi, and P. Vincenzini. 1984. A diffusion model for the oxidation of hot pressed Si_3N_4-Y_2O_3-SiO_2 materials. J. Mater. Sci., Vol. 19, p. 4029.

Boehm, H. P. 1966. Chemical identification of surface groups. Adv. Catalysis, Vol. 16, p. 179.

Bolger, J. C., and A. S. Michaels. 1968. Interface Conversion for Polymer Coatings. P. Weiss and P. G. Cheever (eds.). New York: Elsevier.

Bolster, R. M., and I. L. Singer. 1981. Surface hardness and abrasive wear resistance of ion implanted steels. ASLE Trans., Vol. 24, pp. 526-532.

Bolster, R. M., and I. L. Singer. 1984. Polishing Wear Studies of Coating Materials. In Mechanical Properties, Performance, and Failure Modes of Coating, pp. 201-207. P. R. Shives and M. B. Peterson (eds.). Cambridge, Massachusetts: Cambridge University Press.

Bouarroudj, A., P. Goursat, and J. L. Besson. 1985. Oxidation resistance and creep behavior of a silicon nitride ceramic densified with Y_2O_3. J. Mater. Sci., Vol. 20, p. 1150.

Bowdon, F. P., and D. Tabor. 1964. The Friction and Lubrication of Solids. Oxford, England: Clarendon Press.

Buckley, D. H. 1972. Friction and wear of ceramics. Amer. Cer. Soc. Bull. Vol. 51, p. 884.

Buckley, D. H., and K. Miyoshi. 1985. Fundamental tribological properties of ceramics. Cer. Eng. and Sci. Proceedings, Vol. 6, p. 919.

Campelo, J. M., A. Garcia, J. M. Gutierrez, D. Luna, and J. M. Marinas. 1984. Electron transfer sites on $AlPO_4$, $AlPO_4$-SiO_2, and $AlPO_4$-Al_2O_3 Catalysts. Colloids and Surfaces, Vol. 8, p. 353.

Ching, W. Y. 1982. Phys. Rev. B., Vol. 26, p. 6610.

Ciraci, S., and I. P. Batra. 1983. Phys. Rev. B., Vol. 28, p. 982.

Deryagin, B. V., N. A. Krotova, and V. P. Smilga. 1978. Studies in Soviet Science: Adhesion of Solids. Consultants Bureau. New York: Plenum Press.

Dayan, M. 1985. AES and LEED study of the zinc-blend SiC (100) surface. J. Vac. Sci. Tech., Vol. A3, p. 361.

Dutta, S., and B. Bazek. 1984. Microstructure strength and oxidation of a
10 wt. % Zyttrite-Si$_3$N$_4$ ceramic. J. Amer. Cer. Soc., Vol. 67, p. 89.

Fischer, T. E. 1974. Catalysis and surfaces. J. Vac. Sci. Tech., Vol. 11,
p. 252.

Fischer, T. E., and H. Tomizawa. 1985. Interaction of tribochemistry and
microfracture in the friction and wear of silicon nitride. Wear,
Vol. 105, p. 29.

Fischer, T.E., M. P. Anderson, S. Jahanmir, and R. Salher. 1987. Friction
and Wear of Tough and Brittle Zirconia in Nitrogen, Air, Water,
Hexadecane, and Hexadecane Containing Stearic Acid. In Wear of Materials
1987. Proceedings International Conference on Wear of Materials.
K. Houston and A. Ludema (eds.). New York: American Society of
Mechanical Engineers.

Franks, F. (ed.). 1972. Water--A Comprehensive Treatise, Vol. 1. New York:
Plenum Press.

Fowkes, F. M. 1982. Acid-Base Interactions in Polymer Adhesion, p. 119.
In Microscopic Aspects of Adhesion and Lubrication. J. M. Georges
(ed.). New York: Elsevier.

Frisch, B. 1965. Die hydratation vou OC-Aluminiumoxid. Ber. Dtsch. Keram.
Ges., Vol. 43, p. 149.

Gilroy, D. R., and W. Hirst. 1969. J. Phys. D: Appl. Phy., Vol 2, p. 1974.

Heinicke, G. 1984. Tribochemistry. Munich, Germany: Carl Hauser Verlag.

Hasesawa, H. 1983. Rhombohedral phase produced in abraded surfaces of
partially stabilized zirconia (PSZ). J. Mater. Sci. Lett., Vol. 2,
p. 91.

Iler, R. K. 1979. The Chemistry of Silica, Solubility, Polymerization,
Colloid and Surface Properties, and Biochemistry. New York: John Wiley
and Sons.

Jahanmir, S., and T. E. Fischer. 1986. Friction and Wear of Si$_3$N$_4$ and
ZrO$_2$ Lubricated with Air, Water, Hexadecane, and Stearic Acid. Paper
presented at the ASME-ASLE Tribology Conference in October, 1986.

Katsanis, E. P., and E. Matijevec. 1983. Properties of aluminated silica
sols. Colloid and Polymer Sci., Vol. 261, p. 255.

Knowzinger, H., and P. Ratnasamy. 1978. Catalytic aluminas: surface models
and characterization of surface sites. Catal. Rev.-Sci. Eng., Vol. 17,
p. 31.

Kiehle, A. J., L. K. Heung, P. J. Gielisse, and T. J. Rockett. 1974.
Oxidation behavior of hot pressed Si$_3$N$_4$. J. Amer. Cer. Soc.,
Vol. 58, p. 235.

Kingery, W. D., H. K. Bowen, and D. R. Ulhmann. 1976. Introduction to Ceramics. New York: John Wiley and Sons.

Latanision, R. M., and J. T. Fourie (eds.). 1977. Surface Effects in Crystal Plasticity. Proceedings of NATO Advanced Study Institute. Nordhoff, Leyden, 1975.

Lindberg, L. J., and D. W. Richerson. 1985. Comparison of the contact stress and friction behavior of SiC and ZrO_2 materials. Cer. Eng. and Sci. Proc., Vol. 6, Nos. 7,8, pp. 1059-1066.

Michalske, T. A., and B. C. Bunker. 1984. Slow fracture model based on strained silicate structures. J. Appl. Phys., Vol. 56, p. 2686.

Miyoshi, K., and D. H. Buckley. 1980. Changes in Surface Chemistry of Silicon Carbide (0001) Surface with Temperature and Their Effect on Friction. NASA Technical Paper 1756. Washington, D.C.: National Aeronautics and Space Administration.

Miyoshi, K., and D. H. Buckley. 1982. XPS, AES, and friction studies on single crystal silicon carbide. Appl. Sur. Sci., Vol. 10, p. 35.

Natarajan, C., P. B. Abel, and R. W. Hoffman. 1985. Local structure of silicon films and silicon carbide by surface extended energy loss fine structure. J. Vac. Sci. Tech., Vol. A3, p. 1309.

Posner, G. H., and D. Z. Rogers. 1977. J. Amer. Chem. Soc., Vol. 99, p. 8206.

Regazzoni, A. E., M. A. Blesa, and A. J. G. Maroto. 1983. Interfacial properties of zirconium dioxide and magnetite in water. J. Colloid Interface Sci., Vol. 92, p. 560.

Rehbinder, P. A. 1928. Reports to the VI Congress of Physicists, Moscow 29.

Shimura, H., and Y. Tsuya. 1977. Effects of Atmosphere on the Wear Rate of Some Ceramics and Cermets, p. 452. In Wear of Materials 1977. New York: American Society of Mechanical Engineers.

Singhal, S. C. 1976. Effect of water vapor on the oxidation of hot-pressed silicon nitride and silicon carbide. J. Amer. Cer. Soc., Vol. 59, p. 81.

Smyth, J. R., and D. W. Richerson. 1983. High temperature dynamic contact behavior of sintered alpha silicon carbide. Cer. Eng. and Sci. Proc., Vol. 4, pp. 663-673.

Strehlow, W. H., and E. L. Cook. 1973. J. Phys. Chem. Ref. Data., Vol. 2 p. 163.

Sung, N. H., and C. S. P. Sung. 1980. SPI Proceedings, Vol. 23-B.

Suzuki, A., H. Ashida, N. Furui, K. Mameno, H. Matsunami. 1982. Thermal oxidation of SiC and electrical properties of Al-SiO$_2$-Si MOS structures. Jap. J. Appl. Phys., Vol. 21, p. 579.

Tanabe, K. 1970. Solid Acids and Bases. Tokyo, Japan: Kodansha and New York: Academic Press.

Tomizawa, H., and T. E. Fischer. 1986. Friction and Wear of Silicon Nitride at 150°C to 800°C. ASLE Trans., Vol. 29, No. 4. Park Ridge, Illinois: American Society of Lubrication Engineers.

Tossel, J. A. 1975. J. Am. Chem. Soc., Vol. 19, p. 4840.

Wallbridge, N., D. Dowson, and E. W. Roberts. 1983. The Wear Characteristics of Sliding Pairs of High Density Polycrystalline Aluminum Oxide Under Both Dry and Wet Conditions. In Wear of Materials 1983. New York: American Society of Mechanical Engineers.

Westwood, A. R. C. 1974. Tewksbury Lecture: Control and Application of Environment-Sensitive Fracture Processes. Mat. Sci., Vol. 9, No. 11, pp. 1871-1895.

Wiese, G. R. 1973. Surface Reactions and Electrical Double Layer Properties of Ceramic Oxides in Aqueous Solution. SM Thesis, Massachusetts Institute of Technology.

Wu, C. C., K. R. McKinney, R. W. Rice, W. J. McDonough, and S. W. Freiman. 1981. Oxidation weight gain and strength degradation of Si$_3$N$_4$ with various additives. J. Mater. Sci., Vol. 16, No. 11, pp. 3099-3104.

Chapter 6

SURFACE CHARACTERIZATION METHODS RELEVANT
TO THE TRIBOLOGY OF CERAMICS

Many surface analytical tools are currently available. An estimated 70
to 100 different techniques can be used to examine surfaces and surficial
layers. These techniques provide various types of information on surface
micro-topography, crystallography, or chemical composition. There is
considerable overlap in the information that can be derived from these
techniques; also, some differ from others in relatively minor aspects of
their methodology and information output. Those most useful to the
tribologist are discussed here.

Some of the older methods of examining surfaces and surficial regions
should not be ignored in the rush to employ the most recent surface
analytical techniques. This is especially true in the tribological studies
of ceramics. In fact, because most ceramics are electrical insulators, they
pose certain problems to the analyst employing some of the very surface-
sensitive techniques of electron and ion spectroscopy.

The obvious, traditional techniques that can be very useful in the
study of ceramics are optical microscopy, x-ray diffraction (XRD), x-ray
fluorescence (XRF), and stylus profilometry. XRD and XRF are not really
surface-sensitive because the spectral information derived is from a
surficial region whose depth depends on the energy of the analyzing x-ray
beam and absorbance of the specimens, but typically is on the order of 0.02
mm in depth. These methods obviously are not for monolayer analysis, but
the surficial region probed is also of great interest to the tribologist
because, for example, Hertzian stresses, load- and friction-induced plastic
deformation, recrystallization layers, residual stresses, and products of
surface-initiated chemical reactions are all frequently present. All of the
traditional techniques mentioned can be used in an air atmosphere, while the
electron and ion beam techniques usually require a vacuum environment.

The analytical methods discussed in this chapter are classified as
(a) traditional methods such as x-ray diffraction, optical microscopy, and
stylus profilometry; (b) well-established electron beam analysis techniques
such as scanning electron microscopy (SEM), low-energy electron diffraction
(LEED), Auger electron spectroscopy (AES), and x-ray photoelectron

57

spectroscopy (XPS); (c) ion beam analysis techniques such as ion scattering spectroscopy (ISS) and secondary ion mass spectroscopy (SIMS); and (d) electron energy loss spectroscopy (EELS) and tunneling microscopy. Table 6-1 provides a list of analytical techniques and their acronyms used here.

Table 6-1   Analytical Technique Acronyms

AES	Auger electron spectroscopy
APS	Appearance potential spectroscopy
EDS	Energy-dispersive spectroscopy
EELS	Electron energy loss spectroscopy
ELL	Ellipsometry
ELS	Energy loss spectroscopy
EM	Electron microprobe
EMXA	Electron microprobe x-ray analyzer
EXAFS	Extended x-ray absorption fine structure
FIM	Field ion microscopy
IMP	Ion microscopy analysis
ISS	Ion scattering spectroscopy
LEED	Low-energy electron diffraction
RBS	Rutherford back-scattering
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectroscopy
STEM	Scanning transmission electron spectroscopy
UPS	Ultraviolet photoelectron spectroscopy
XF	X-ray fluorescence
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

INSTRUMENTATION AND APPLICATIONS

Traditional Methods

The importance of the type of information that can be obtained by x-ray diffraction is well known. This information, which includes crystallography, grain size, stress distribution, and glass-phase detection, is of obvious importance in the tribological behavior of ceramics and does not require elaboration here.

Optical microscopy is also of obvious value, but some of the specialized techniques of great value in studying mechanisms of both liquid and solid lubrication should be mentioned. The information explosion in the 1960s and 1970s concerning the mechanisms of elastohydrodynamic lubrication with oils was to a significant extent due to the use of optical interferometric microscopy. With this method, it is possible to determine the lubricant film

thickness distribution and pressure distribution within a lubricant contact (Foord et al., 1968; Wedeven et al., 1971). When combined with infrared microscopy, the method can be used to determine temperature distribution within a lubricated, concentrated contact (Griffioen and Winer, 1986; Nagaraj et al., 1978; Winer, 1979). In addition, the infrared emission spectra from a Hertzian contact can be recorded and analyzed to obtain information about the chemical composition of the lubricant film (Lauer and Peterkin, 1975). The optical techniques have an advantage in allowing measurements to be made in air; vacuum is not required.

Figure 6-1 is a schematic diagram of an optical metallograph combined with a tribometer for the study of Hertzian contacts. When rolling or sliding is initiated, an oil film is formed in the contact and the color distribution (due to optical interferonic effect) can be used to compare film thickness distribution. The behavior of solid lubricants, abrasive ceramic particles, and unlubricated glass within concentrated contacts can also be studied with this apparatus (Sliney, 1978).

Stylus profilometry is also of obvious value but is sometimes damaging to the film because it is a contact technique. Several noncontact techniques are now available. One of these is tunneling microscopy, which is discussed in a later section.
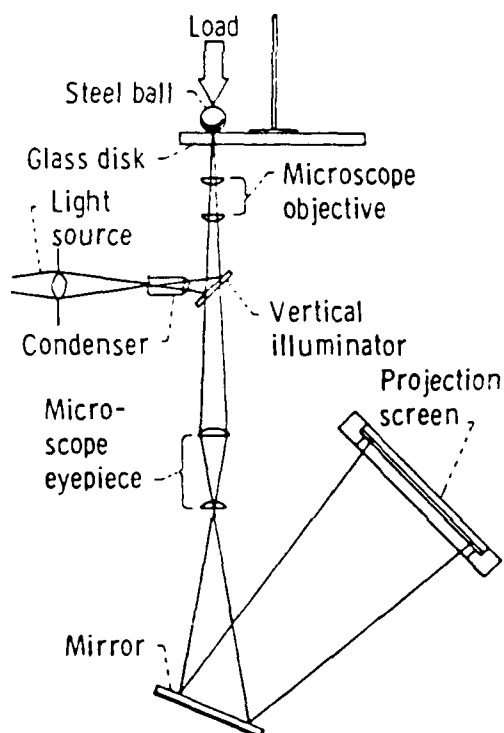

FIGURE 6-1 Schematic diagram of optical system (Sliney, 1978).

Electron Beam Analysis

Scanning electron microscopy (SEM) is a basic tool for the tribologist. Combined with energy-dispersive spectroscopy (EDS), it can give invaluable information on surface morphology and on composites. Figure 6-2 shows examples of SEM and x-ray dot maps that give the element distribution in a metal-nonmetal composite (Jacobson and Young, 1982). Ceramics tend to "charge-up" in the SEM and therefore are usually coated with an extremely thin metallic or carbon film. The EDS technique probes to a sufficient depth to obtain elemental analysis of the ceramic substrate. Scanning transmission electron spectroscopy (STEM) is a useful variation of electron microscopy for examining thin sections.

Low-energy electron diffraction (LEED) is a well-established surface-sensitive technique. Because the incident beam is low energy (40 to 400 eV), structural (crystallographic) information can be obtained for monolayer surface films. Figure 6-3 shows a schematic diagram of a LEED instrument combined with an adhesion experiment. Figure 6-4 is an example of LEED patterns for a clean iron surface compared with an iron surface with an absorbed monolayer of methane (Buckley, 1970). Unfortunately, LEED can only be used with difficulty or not at all for insulators such as ceramics because they readily assume an electrostatic charge in an electron beam; since the incident beam is of very low energy, conductive coatings do not appear to be a solution. However, LEED is applicable to conductive ceramics such as silicon carbide and semiconductor solid lubricants such as molybdenum disulfide. Another limitation of LEED is that its use is limited for the most part to the study of single crystals.

Auger Electron Spectroscopy

AES is also a surface-sensitive technique. It uses an electron beam typically of the 1 to 5 keV energy and probes slightly deeper than LEED. AES gives composition rather than structural information. Probe depths can be several monolayers below the surface, but the technique is sensitive to a fraction of a monolayer. Auger analysis yields elemental composition and some information on the chemical bond state of those elements. The use of AES to analyze insulators presents experimental difficulties because of electrostatic charging, but procedures have been developed for obtaining spectra of insulators, including glass. Goldstein and Carlson (1972) give excellent examples of glass spectra before and after sputter etching that show significant differences in the surface composition compared to the near-surface (surficial) layer composition.

Figure 6-5 is a schematic diagram of a combined Auger system and a pin-on-disk tribometer (Buckley, 1973). This combination allows surface analysis of a spot on the disk wear track immediately after it exits the sliding contact, thus minimizing changes in surface composition that could occur in transferring wear specimens from a tribometer to a separate Auger system. An incidental benefit of analyzing a moving surface, which is applicable as well to nontribological studies, is that problems of electrostatic charging are reduced by presenting an ever-changing target area to the incident electron beam.
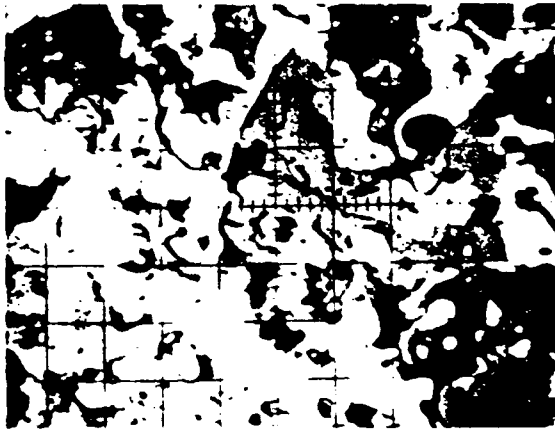
(a) Backscatter electron photograph.
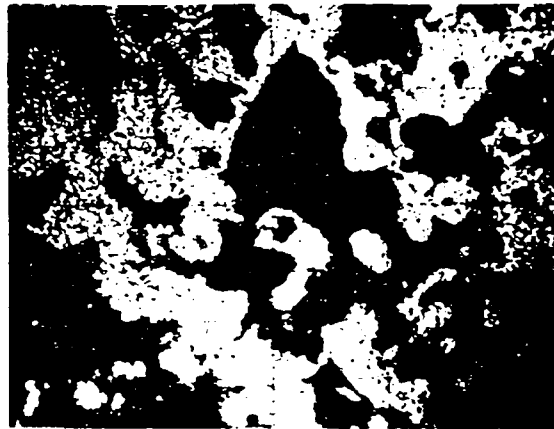
(b) Silver X-ray photograph.
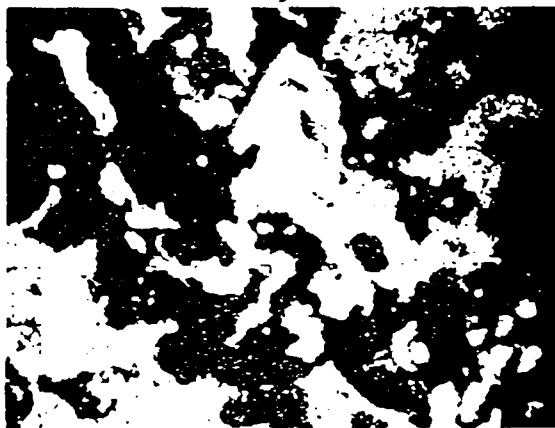
(c) Nickel X-ray photograph.
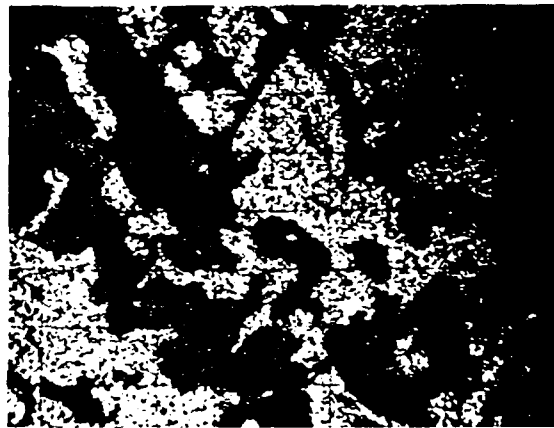
(d) Chromium X-ray photograph.
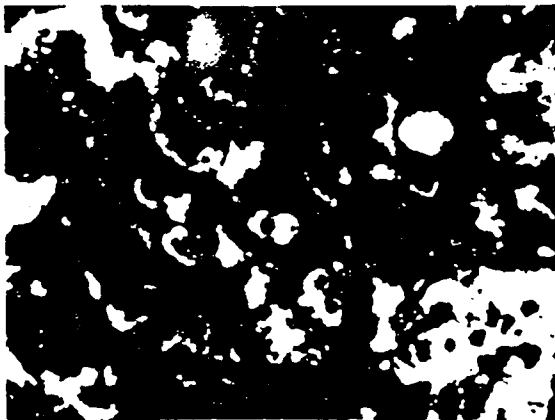
(e) Calcium X-ray photograph.
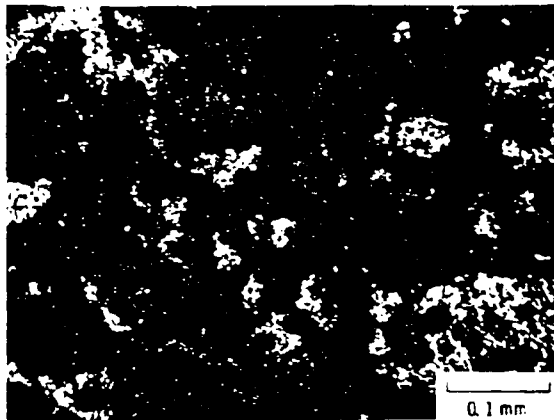
(f) Fluorine X-ray photograph.

0.1 mm

FIGURE 6-2 EMXA photographs showing elemental distribution in NASA LUBE PS10$_6$ coating 1 (with 1.25 wt percent AIPO$_4$) (Jacobson and Young, 1982).
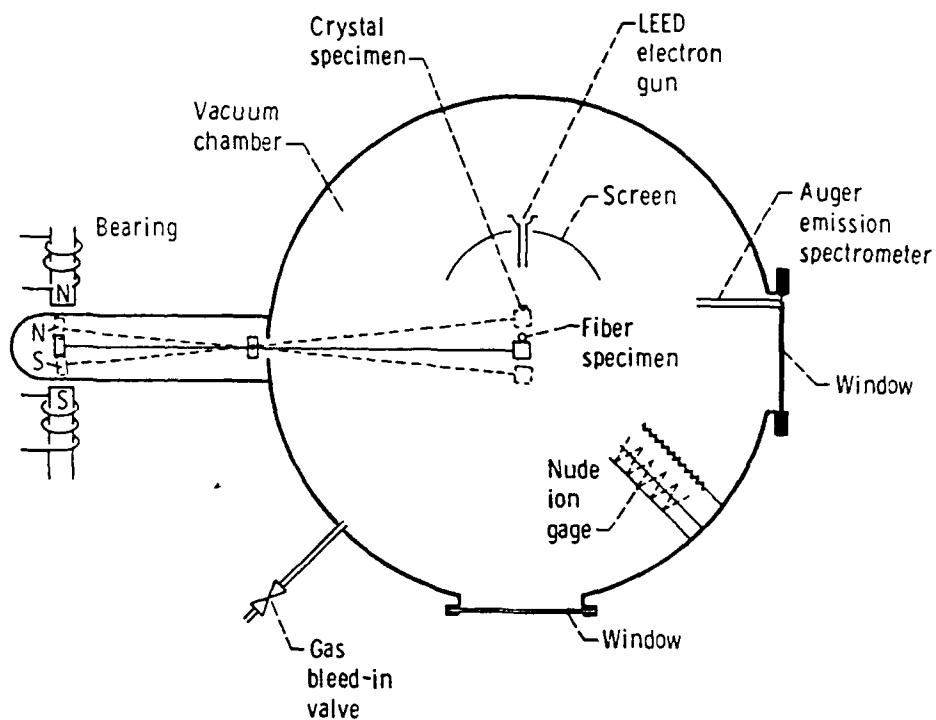
FIGURE 6-3   LEED adhesion apparatus (Buckley, 1970).

(a)   clean iron (001) surface
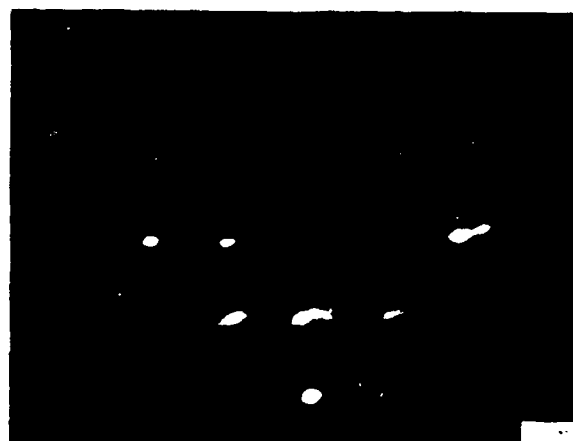
(b)   methane-covered iron (001) surface

FIGURE 6-4   LEED patterns for an iron (001) surface (a) in the clean state and (b) with a monolayer of methane present (Buckley, 1970).

X-ray photoelectron spectroscopy (XPS) differs from AES in that
it employs monoenergetic (usually soft) x-rays to excite emission of
characteristic photoelectrons from the specimen surface. The energies of
the emitted electron are characteristic of the elements present and their
chemical bond states. Compared to Auger, XPS gives more complete and more
easily interpreted information on chemical bond states. For example, sulfur
can be identified as elemental sulfur, sulfide, sulfate, etc. XPS can also
be combined with a tribometer in a vacuum system.

Figure 6-6 gives the XPS spectra for silicon carbide in vacuum at various
temperatures (Buckley and Miyoshi, 1985). The ability of XPS to detect bond
states enables the analyst to differentiate carbon as amorphous carbon,
graphite, or carbide from the binding energies of the carbon peaks in the
spectra. In this example, it is clear that the amorphous carbon initially
present disappears with increasing temperature, and graphite appears at the
surface. This has been interpreted to mean that silicon carbide dissociates
at high temperature to graphite and to elemental silicon, which sublimes
away.

Ion Beam Analysis

Ion scattering spectroscopy (ISS) and secondary ion mass spectroscopy
(SIMS) utilize analyses by mass spectrometry, in contrast to the previously
discussed techniques that utilize electron spectroscopy. An ion spectroscopy
schematic diagram is shown in Figure 6-7 (Ferrante, 1982).

In principle, ISS is extremely simple. A beam of ions is aimed at a
surface at an oblique angle and the scattered ions are energy-analyzed to
give the mass of surface ions from which they elastically scattered. The
technique is surface-sensitive and gives elemental and quantitative
information.

Ion scattering can be used to some extent as a channeling technique to
probe very thin films in depth (Van Loenen et al., 1984) Ions scattered from
the surface will have a slightly different energy from those scattered from
the film-substrate interface. The energy peaks will not be totally resolved
in the spectra but can be mathematically resolved into their component peaks.

SIMS is very surface-sensitive and is capable of analyzing organic
molecular groupings on a surface. Research results have been reported
(Campana et al., 1981), for example, that demonstrate the usefulness of this
tool for adsorption and desorption studies of organics on bearing materials.

Electron energy loss spectrometry (EELS) is a high-resolution
surface-sensitive analytical tool that provides information about the
vibrational motion of surface atoms and molecules under ultrahigh-vacuum
conditions. The technique literally generates infrared spectra of the
surface. Figure 6-8 is a schematic diagram of an EELS system. A mono-
energetic beam of electrons is impinged upon the sample surface, where it
interacts with surface atoms and molecules to excite their characteristic
vibrational motion. In so doing, the incident electrons lose energy in a
manner quantitatively related to the characteristic vibrations of the surface
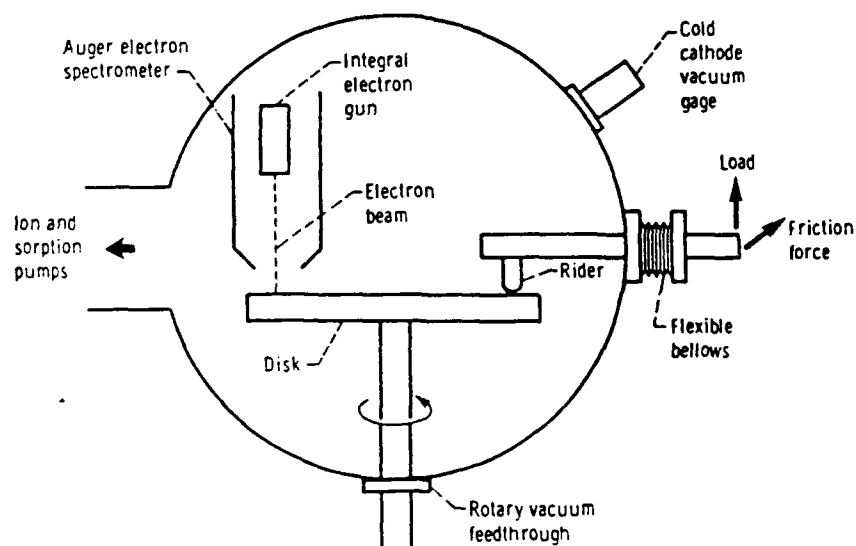
FIGURE 6-5 Friction apparatus with Auger electron spectrometer (Buckley, 1973).
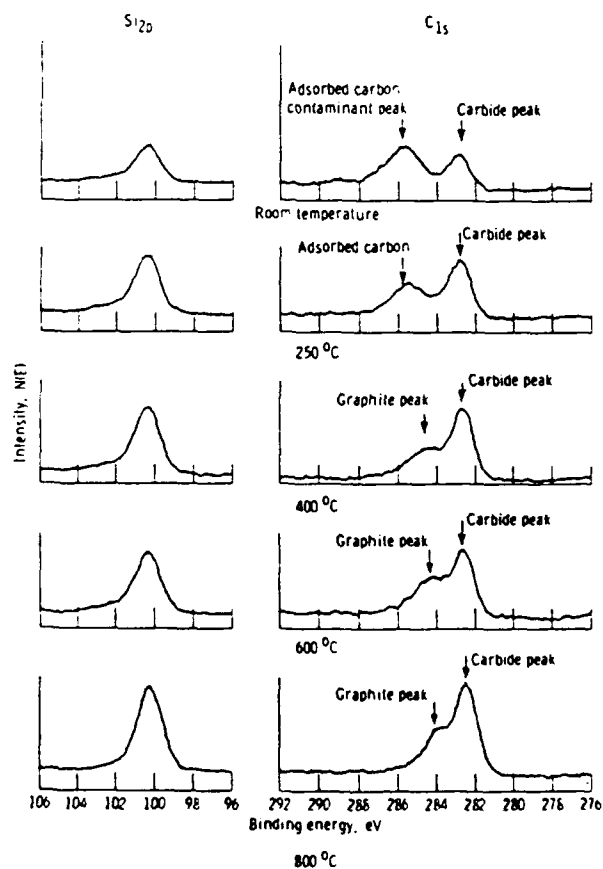
FIGURE 6-6 Representative Si_{2p} and C_{1s} XPS peaks on SiC surface preheated to 800°C (Buckley and Miyoshi, 1985).
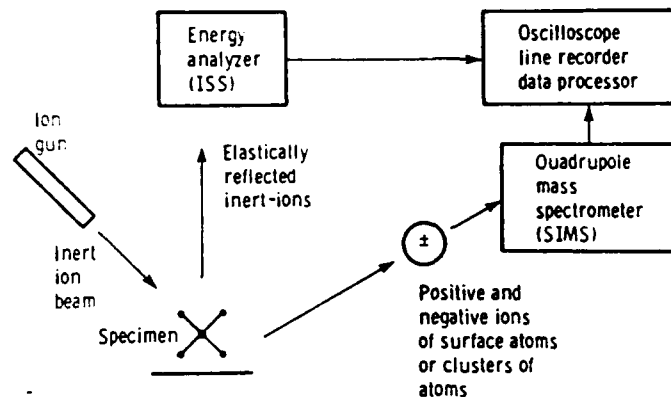
FIGURE 6-7 Outline of the ISS/SIMS surface analyzing system (Ferrante, 1982). (Reprinted by permission of the American Society of Lubrication Engineers. All rights reserved.)
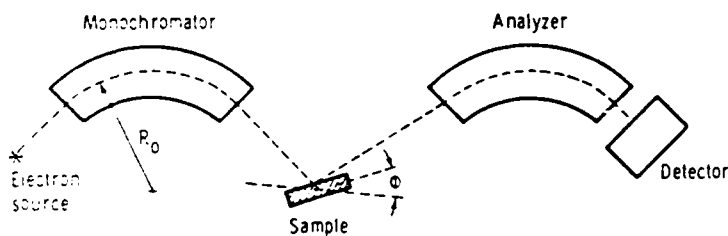
FIGURE 6-8 Schematic diagram of an electron energy loss experiment. Electrons from a cathode pass through a monochromator and strike the sample, and the energy spectrum of the scattered electrons is probed by a second monochromator.

species. The exciting beam therefore contains information about the surface vibrational states.

An elegant example of an EELS experiment was reported by Waclawski (1982). The energy loss spectra of diamond before and after heating to 1000°C in ultrahigh vacuum are shown. The "as-polished" diamond contains peaks for vibrational modes characteristic of the hydrogen-to-carbon bond, literally hydrocarbon (HC) bonds. After heating and hydrogen desorption, the HC peaks are no longer present. This correlates with studies reported by Pepper (1982) concerning the effect of temperature on the friction of copper sliding on diamond. Below about 800°C friction was low, but it rose sharply at higher temperatures. Pepper was able to relate this phenomenon both

theoretically and experimentally to changes in the electron surface state of the diamond caused by thermal desorption of hydrogen.

EELS is most applicable to surface studies of single-crystal conductors and semiconductors. However, the use of a secondary electron gun to control charging effects enables one to also study insulating materials (Pireaux, 1985).

HYDROGEN DETECTION

As stated in Chapter 5, hydration phenomena of ceramics are widespread and important; they require the ability to detect water, OH radicals, and hydrogen on and below the ceramic surface.

EELS may be an especially valuable analytical tool for ceramics because of its ability to detect hydrogen. The tribology of ceramics is sensitive to the presence of hydrogen and its state of chemical combination on the surface. Other techniques with some potential for distinguishing between atomic hydrogen, hydroxyl, water, and hydrocarbon species include the following: secondary ion mass spectroscopy (SIMS) with a reliable means of compensating for charge effects; emission infrared spectroscopy; and Raman spectroscopy.

The tunneling microscope is a noncontact method of surface profilometry. An electron emitter with a typical radius of 100 to 10,000 Å is brought close to a conducting surface while a contact current is passed through the emitter. The field strength is related to the emitter-to-surface spacing. The emitter is swept across the surface by two piezoelectric elements. The emitter is mounted on a third piezoelectric element that moves the emitter in the z-axis during the sweep. The z-axis movement maintains a constant spacing via a feedback circuit that maintains constant current. As the emitter rasters the surface, an xy topographic representation of the surface is recorded.

Young and coworkers (1972) reported a degree of resolution adequate to provide the topographic map of a diffraction grating with 180 lines per mm spacing. Currently, resolution is sufficient to depict individual atoms and their arrangements on a surface (Becker et al., 1985). Again, this method will require special techniques, if applicable at all, to be used on insulating ceramics.

COMPARISONS OF CHARACTERIZATION TECHNIQUES

As noted earlier, traditional techniques such as optical microscopy and x-ray diffraction can be used in an air atmosphere, whereas the electron and ion beam techniques usually require a vacuum environment. Charged particle beams produce electrostatic charges on the surface of insulating materials, such as most ceramics. Notwithstanding the problems associated with electron and ion beam techniques in the study of ceramics, some of these can provide extremely valuble information. Rapid progress is also being made in circumventing some of the inherent problems, such as electrical charge buildup on specimens of insulator materials.

The most common indispensable electron beam method is scanning electron microscopy (SEM). The problem of charge build-up is easily solved by coating insulator specimens with a thin film of a conducting material such as graphite or vapor-deposited gold. SEM has the advantages of excellent depth of focus (rough surfaces may be examined) and very high magnification capability. SEM requires that the specimen have some composition or topographical variation on the specimen surface in order to produce a sharp image of sufficient contrast. Therefore, a very smooth surface of uniform composition will produce a featureless image on SEM. SEM also requires a vacuum atmosphere in the specimen chamber. Optical microscopy should therefore be used as a complimentary tool to SEM. Often surfaces that are featureless on SEM show very good contrast on an optical microscope. Conversely, the optical microscope requires a very smooth surface and is usually unsatisfactory except at low magnification on the relatively rough surfaces characteristic of wear areas.

Of the truly surface-sensitive analytical tools available, probably the most useful to the tribologist are Auger electron spectroscopy, x-ray photoelectron spectroscopy, ion scattering spectroscopy, and secondary ion mass spectroscopy.

AES is capable of identifying all elements except hydrogen and helium. It can detect surface species present in a concentration of as little as 1/100 of a monolayer. It can provide limited information on the state of combination of surface elements. For example, it can differentiate carbon present as CO, amorphous carbon, or graphite.

XPS is more powerful than AES in providing information on molecular composition (compound identification). This technique employs a monochromatic x-ray beam for excitation of surface atoms to emit photoelectrons of characteristic energies. These characteristic energies are related to the binding energies of the surface atoms from which, in turn, the nature of surface molecules can be deduced. Calibrations can be done from theoretical considerations or directly from spectra of known compounds. In comparing AES and XPS, it can be said in general that AES has better surface spatial resolutions (much smaller target spot size) and can provide superior fine detail, while XPS averages over a large area but provides more molecular information. Both methods can be coupled with sputtering to provide depth profiling capability.

ISS is one of the most surface-sensitive techniques, has relatively low resolution, especially for high ion mass numbers, and results can be difficult to interpret. However, it is of interest because of its extreme surface sensitivity. SIMS differs in detail from ISS in that, while scattering of a primary beam by a surface is analyzed in ISS, the emission of secondary ions produced by a primary ion beam are analyzed in SIMS.

One of the primary limitations of the truly surface-sensitive methods is related to that very sensitivity: the analyses must be performed in vacuum. (The presence of an air path would interfere with the emitted electrons or ions before they could reach the detectors.) However, "post facto" studies of wear specimens run in an air or other "dirty" atmosphere can yield much useful information. Of course, the analyst must consider the possibility

that the surface analyzed may not be exactly the same composition as it was in situ. Dynamic analysis in situ during an experiment is always desirable but not always practical.

The electrical charging of insulators such as most ceramics during analyses by electron or ion beam techniques can sometimes be circumvented by adjusting primary beam energies and angles of incidence to give a stable charge on the surface. This charge can then be "stripped out" as background. It is a varying charge that is difficult to deal with. In the case of ion beam techniques, the surface charge can be positive and therefore neutralized with a carefully controlled auxiliary electron beam.

A comparison of the capabilities of many surface analytical techniques is given in Table 6-2.

SUMMARY

The capabilities among existing surface analytical tools enable the tribologist to study much of the chemical and physical phenomena that occur during the friction and wear process. Much can be learned about tribochemical effects that are of primary importance to the friction and wear processes. The best experimental approach is to perform the analyses during the friction process. A limitation with the sensitive electron and ion beam techniques is that dynamic studies of this sort can only be performed in a vacuum. Post-experiment analyses can be useful but can also be misleading if proper consideration is not given to the possibility of changes in surface composition when the specimen is transposed from the friction apparatus to the analytical instrument. Therefore, there is a trend toward unified designs whereby the specimens can be rapidly transferred from the tribometer to the analytical chamber without removing them from the apparatus. This does not eliminate the problem, of course, but it certainly minimizes it.

The problem of electrostatic charging of nonconducting specimens subjected to electron and ion beam analytical probes was discussed previously. There is currently a strong trend among surface scientists to find ways to deal with it. Considerable progress has been made, and analyses that were considered impossible as little as a year ago can now be performed. More research is necessary to put the analyses of ceramics by charged beam techniques on a routine basis.

A serious limitation is the difficulty in using beam techniques to reveal the presence of hydrogen and hydroxyl or water molecules on the surface. Electron energy loss spectroscopy has been mentioned as one technique for hydrogen detection. Other possibilities are optical techniques such as emission infrared spectroscopy and Raman spectroscopy.

Anticipated future trends include the increasing use of electron energy loss spectroscopy and possibly ion tunneling techniques. An interesting pioneering study is being conducted at NASA's Lewis Research Center on possible uses of acoustic microscopy in tribological studies.

TABLE 6-2   Widely Used Techniques for Surface Analysis

Technique	Surface-Sensitive	Commercially Available	Analysis of Practical Systems	Elemental Analysis	Compound	Quantitative
1. Elemental and chemical results by electron levels						
AES	Yes	Yes	Yes	Yes	To a degree	To a degree
APS	Yes	No	Yes	Yes	No	To a degree
EM	No	Yes	Yes	Yes	No	Yes
XF	No	Yes	Yes	Yes	No	Yes
XPS	Yes	Yes	Yes	Yes	Yes	Yes
2. Chemical and elemental analysis by mass						
ISS	Yes	Yes	Yes	Yes	No	To a degree
RBS	No	Yes	Yes	Yes	No	Yes
SIMS	Yes	Yes	Yes	Yes	To a degree	To a degree
IMF	No	Yes	Yes	Yes	No	Yes
3. Elemental analysis by vibrational state						
ELS	Yes	Yes	No	No	No	No
4. Structural analysis, macroscopic features						
SEM	Yes	Yes	Yes	Yes	No	No
ELL	Yes	Yes	Yes	No	No	No
5. Structural analysis, microscopic						
EXAFS	Yes	No	Yes	No	No	No
LEED	Yes	Yes	No	No	No	No
FIM	Yes	Yes	No	Yes (with an atom probe)	To a degree	No

Useful analytical techniques are in place. They are constantly being improved, but new ones are needed, especially for the analysis of hydrogen and hydrogen radicals.

RECOMMENDATIONS

Surface Characterization

The following recommendations are directed toward acquiring new knowledge of analytical systems for characterizing ceramic surfaces:

- Investigate improved methods for detecting light elements, especially hydrogen and its chemical radicals and compounds (e.g., hydroxyl, water, etc.).

- Develop techniques for in situ analyses of ceramic wear surfaces during tribological experiments.

- Investigate techniques that do not require a vacuum (e.g., optical techniques such as FTIR, Raman, etc.).

- Explore methods such as the use of a small spot ESCA device with an atmosphere working chamber connected to a vacuum analytical chamber via interconnect locks for rapid transfer of specimens from working environments to an analytical chamber within the same apparatus.

REFERENCES

Becker, R. S., et al. 1985. Tunneling Images of Germanium Surface Reconstruction and Phase Boundaries. Phys. Rev. Let., Vol. 54, No. 25, pp. 2678-2680.

Buckley, D. H. 1970. Interactions of Methane, Ethane, Ethylene, and Acetylene with Ion (100) Surface, Report No. TN D-5822 (May). Washington, D.C.: National Aeronautics and Space Administration.

Buckley, D. H. 1973. Friction-Induced Surface Activity of Some Hydrocarbons with Clean and Oxide-Covered Iron, Report No. TN D-7233. Washington, D.C.: National Aeronautics and Space Administration.

Buckley, D. H., and K. Miyoshi. 1985. Fundamental Tribological Properties of Ceramics, Report No. TM-86915. Presented at the 9th Annual Conference on Composites and Advanced Ceramic Materials. Columbus, Ohio: American Ceramic Society.

Campana, J. E., et al. 1981. Characterization of polymeric thin films by ion-damage secondary ion mass spectrometry. Appl. Sur. Sci., Vol. 8, pp. 337-342.

Ferrante, J. 1982. Practical applications of surface analytical tools in tribology. Lubrication Engineering, Vol. 38, No. 4, pp. 223-236.

Foord, C. A., W. C. Hammann, and A. Cameron. 1968. Evaluation of lubricants using optical elastohydrodynamics. ASLE Trans., Vol. 11, No. 1, pp. 31-39.

Goldstein, B., and D. E. Carlson. 1972. Determination of the composition of glass surfaces by Auger spectroscopy. J. Am. Cer. Soc., Vol. 55, No. 1, p. 51.

Griffioen, J., and W. O. Winer. 1986. Infrared Surface Temperature Measurements. In Sliding Ceramic-Ceramic Contact. Proceedings of the 1985 Leeds-Lyon Symposium.

Jacobson, T. P., and S. G. Young. 1982. Effect of aluminum oxide additions on composition of three-component plasma-sprayed solid lubricant, Report No. TP 1990 (March). Washington, D.C.: National Aeronautics and Space Administration.

Lauer, J. J., and M. E. Peterkin. 1975. Infrared emission spectra of fluid films by Fourier transform spectroscopy. American Laboratory, Vol. 7, No. 11, pp. 27-33.

Nagaraj, H. S., D. M. Sanborn, and W. O. Winer. 1978. Direct surface temperature measurement by infrared radiation in EHD and the correlation with the blok flash temperature theory. Wear, Vol. 49, pp. 43-59.

Pepper, S. V. 1982. Effects of electronic structure of the diamond surface on the strength of the diamond-metal interface. J. Vac. Sci. and Tech., Vol. 20, No. 3, pp. 643-646.

Pireaux, J. J., et al. 1985. Surface structure of (100) LiF and (100) NaCl investigated by high resolution electron energy loss spectroscopy. Sur. Sci., Vol. 162, pp. 132-137.

Sliney, H. E. 1978. Dynamics of solid lubrication as observed by optical microscopy. ASLE Trans., Vol. 21, No. 2, pp. 109-117.

Van Loenen, E. J., M. Iwami, R. M. Tromp, and J. F. Van der Veen. 1984. The Adsorption of Ag on the Si (111) 7x7 Surface at Room Temperature Studied by Medium Energy Ion Scattering, LEED, and AES. Amsterdam, the Netherlands: FOM Institute for Atomic and Molecular Physics.

Waclawski, B. J., et al. 1982. Direct verification of hydrogen termination of the semi-conductor diamond (111) surface. J. Vac. Sci. and Tech., Vol. 21, p. 368.

Wedeven, L. D., D. Evans, and A. Cameron. 1971. Optical analysis of ball bearing starvation. J. of Lubrication Tech. (July), pp. 349-363.

Winer, W. O. 1979. A review of Thermal Phenomena in EHD, pp. 125-130. Proceedings of the 1978 Leeds-Lyon Conference. London: Mechanical Engineering Publications.

Young, R., et al. 1972. The topographiner: an instrument for measuring surface micrography. The Review of Sci. Instr., Vol. 43, No. 7, p. 999.

SUGGESTED ADDITIONAL READING

Buckley, D. H. 1983. Application of Surface Analytical Tools in the Investigation of Surface Deterioration Processes, Report No. TM X-83452. Paper presented at the Surtek-Kongress '83, Berlin, West Germany, October, 1983. Washington, D.C.: National Aeronautics and Space Administration.

Evans, A. G., and D. B. Marshall. 1981. Wear Mechanisms in Ceramics. In Fundamentals of Friction and Wear. D. A. Rigney (ed.). Metals Park, Ohio: American Society for Metals.

Ferrante, J. 1982. Practical applications of surface analytical tools in tribology. Lubrication Eng., Vol. 38, No. 4, pp. 223-236.

Frichette, V. D., W. C. LaCourse, and V. L. Burdich (eds.). 1974. Surfaces and Interfaces of Glass and Ceramics. New York: Plenum Press.

Kane, P. F., and G. B. Larrabee (eds.). 1976. Characterization of Solid Surfaces. New York: Plenum Press.

Chapter 7

FRACTURE PROCESSES AND THE WEAR OF CERAMIC MATERIALS

With the rapidly increasing use of ceramics in structural applications, there is growing interest in the wear behavior of these materials. In particular, erosive and abrasive wear may be limiting factors in certain designs, and these need to be understood quantitatively. Generally, when ceramic materials contain small hard particles, as in erosion and abrasion, both elastic and plastic behavior are observed. Because of the complexity of the elastic-plastic stress fields, there are as yet no complete analyses of the processes of indenting of brittle solids by static or sliding abrasive particles. A considerable amount of experimental and approximate analytical work has been done in this field for the past half century. An understanding of indenting and scratching appears to be a necessary first step in studying wear processes.

EXPERIMENTAL STUDIES OF INDENTATION

Several characteristic crack patterns have been observed to form when brittle solids are loaded by spherical or sharp indenters. For large enough spheres the initial crack appears as a ring around the contact area. With increasing load the crack propagates downward to form the frustum of a cone, and additional concentric ring cracks may appear. Eventually a median crack may occur under the indenter, and at a large enough load the material inside the initial cone crack will shatter. Unloading before this occurs may lead to detachment of material. As the size of the spherical indenter is decreased, the average stress at fracture increases, and eventually plastic flow precedes fracture. For sharp indenters, plastic flow occurs upon loading, and cone cracks are generally not observed. Above a critical indentation size, radial or (Palmquist) cracks are observed on the surface at the corners of the indenter. Median cracks then form at the base of the plastic zone and merge with the radial cracks. Other cracks originating at the plastic zone and propagating almost parallel to the surface are often observed during loading but in other cases have only been observed during unloading. In any event, upon unloading, all types of cracks generally extend. This behavior has been described by Evans and Wilshaw (1976), Lankford (1981), and Lankford and Davidson (1979a and b).

73

THEORETICAL STUDIES OF INDENTATION

Theoretical work has been done on the load to initiate cracks, often referred to as the threshold, and on the subsequent crack extension. Most analyses deal with median and radial cracks, since the prediction of lateral cracking presents greater difficulties.

Initiation Threshold

It appears that, after certain modifications, the spherical cavity solution might be a suitable approach for predicting radial crack initiation, whereas for median cracks the nucleation process is more likely to be the result of shear deformation. Based on these clues, an approach to describe initiation was developed by Chiang and coworkers (1982a). The spherical cavity solution was used to describe the indentation stress field, but to include the free-surface effect, a point-force solution was superimposed on the spherical-cavity solution. Based on this general stress field, the stress field for radial cracks was represented by a polynomial in terms of r, the distance from the crack center (Chiang et al., 1982b). The relationship between load, crack geometry, and material properties was then obtained for radial crack initiation under the Vickers indenter as

$$PH^3/K_c^4 = 10[f(\delta)]^4$$

where P is the indentation load, H is the hardness, and K_c is the fracture toughness of the indented material. The function $f(\delta)$ is

$$f(\delta) = 2(\delta/\pi)^{1/2}[A_0 - (\pi A_1/4)\delta + (2A_2/3)\delta^2 + \ldots]$$

where $\delta = c/a$; a is the radius of the equivalent hemispherical indentation; and A_0, A_1, and A_2 are parameters that depend on the crack system being considered and the relative plastic zone size $\beta = b/a$, where b is the radius of the hemispherical plastic zone. The theoretical results for the radial crack threshold load from this equation compare reasonably well with experiments.

For median cracks, Chiang and co-workers (1982b) considered that nucleation was caused by shear deformations in the plastically deformed zone under the indenter. However, because of the difficulties in knowing the location and the dimension of the shear bands, the discussion was only qualitative. It was found that the threshold load is very sensitive to the ratio of T/Y and $1/b$, where T is the effective shear stress acting along the nucleating shear planes, Y is the uniaxial yield stress, 1 is the length of the slip band, and b is the radius of the hemispherical plastic zone.

Crack Growth

For crack growth, work has been done on median, radial, and lateral cracks under both small spherical indenters and Vickers indenters for various materials. In one approach (Evans and Wilshaw, 1976), the derivation was started from the assumption that the boundary condition at the indenter interface is a constant pressure condition.

Another approach for small spherical indenters was developed for radial cracks for glass (Swain and Hagan, 1976). Here, the indentation stress field was represented by a superposition of the Hertz elastic solution and the stresses about a cylindrical cavity. With this stress field, fracture mechanics was applied, with the assumption that "a suitable flaw is located at about the elastic plastic boundary and that this flaw quickly grows into a fully developed crack..." as stated by Swain and Hagan.

Despite the extensive literature on crack initiation and growth under various types of indenters, it is still necessary to rely on experiment to calibrate the different models.

SCRATCHING

Experimental Studies

Experimentally, work has been done on observing fracture patterns, measuring crack growth, and observing the distribution of stresses around scratching. For crack patterns, observations were reported as early as about half a century ago. With a sharp conical diamond indenter scratching on glass, two types of cracks were observed (Holland and Turner, 1937). One type extended vertically downward under the scratching tool and was named the "median crack." The other cracks, which extended parallel to the surface of the glass, were named "lateral cracks."

In addition to the crack patterns on glass with the sharp conical diamond indenter, the observations of cracking phenomena in scratching have also been made on a variety of materials using Vickers indenters (Swain, 1979). It was found that the crack patterns in scratching were very similar to the ones in quasi-static pointed indentation. The major difference was that the cracks in scratching were asymmetric because of the tangential components of load, and the cracks in indentation were axisymmetric. Again a quantitative relation between crack size and load has to rely on experimental calibration.

WEAR

Ceramic materials that are normally characterized as "brittle" based on bulk mechanical tests show a size effect on strength. That is, as smaller and smaller regions are tested, the average stress at fracture is observed to increase. This phenomenon was explored and treated quantitatively in the pioneering work of Weibull (1939). One consequence of the size effect in wear studies is that, as a surface is loaded by smaller and smaller particles, it will eventually exhibit behavior characteristics of a ductile metal rather than a brittle solid. Presumably, the decreased probability of finding strength-impairing flaws in small regions results in an elevation of the fracture stress above the value required for plastic flow. The transition from "brittle" to "ductile" is observed very easily in erosion testing. Since the variation in weight loss due to erosion as a function of angle of impingement is quite different for brittle and ductile materials (Sheldon and Finnie, 1966a), practically, the important aspect of the transition to ductile behavior is that wear rates decrease dramatically as

this transition occurs. Presumably, the ceramic material is behaving as a ductile metal with an extremely high yield stress. Although the brittle-ductile transition is not as easily demonstrated in abrasive wear, it is found to take place with a similar decrease in wear rate when a transition occurs to ductile behavior. For this reason it is important to identify and understand the factors that lead to a transition to ductile behavior in abrasive and erosive wear.

Models of abrasive and erosive wear based on crack formation and inter-action at and near a surface are usually based on the interaction of an indenter with a smooth semi-infinite solid. While such an idealized picture may be realistic for initial impacts, a question that has yet to be answered is how well this model represents a surface that has been roughened by prior wear. Despite this limitation, the idealized models have been reasonably successful in predicting the relative influence of wear variables (particle size, impact velocity) and material properties (fracture toughness and hardness). However, quantitative prediction of wear rates from first principles is still an unrealized goal.

The earliest models of erosion and abrasion resulting from fracture induced by solid particles were based on spherical indenters (Sheldon and Finnie, 1966b; Oh and Finnie, 1966; Oh et al., 1972; Vaidyanathan and Finnie, 1972). For erosion, the predicted variation of volume removal with particle size and velocity was in reasonable agreement with experiment. Also, it was possible to predict the variation of weight loss in erosion with angle (Oh, 1970) and the approximate particle size at which a transition to ductile behavior would be observed (Sheldon and Finnie, 1966a). This work was based on the stress field under a spherical indenter loaded by normal and tangential forces and the Weibull probabilistic treatment of brittle strength (Weibull, 1939).

In most practical applications, erosive and abrasive wear is due to sharp particles rather than spheres. Intensive research in the past decade has led to a greatly increased understanding of the fracture patterns that occur under sharp indenters, and this information has been incorporated into wear analyses. A greatly simplified description of the cracking process is that initially a plastic zone forms under the indenter. Once a threshold load has been exceeded, which is a function of indenter geometry and materials properties, a median crack will form. Lateral cracks have been reported to form on loading, but primarily they appear to be produced and extended by the residual stress field, which arises when the indenter is removed. Models of erosion based on the depth and radial extent of the lateral cracks have been developed by several workers (Evans and Wilshaw, 1976, 1977; Evans et al., 1978; Ruff and Wiederhorn, 1979). Table 7-1 summarizes the role of particle radius, R; impact velocity, V; plane strain fracture toughness, K_{IC}; and indentation hardness, H, predicted by the various theories. These are all limited to particles making normal impact on the surface. Somewhat surpris-ingly, in view of the various assumptions involved, the prediction of the models do not vary greatly. Also, agreement with experiment is reasonable in view of the approximate nature of the models. Experiments (Sheldon and Finnie, 1966b) on five brittle solids eroded by silicon carbide particles show radius exponents from 3.7 to 4.1 and velocity exponents from 2.65 to 3. Other tests (Gulden, 1979) support the predicted variation of

Vol ~ $K_{IC}^{-1.33}H^{-0.25}$. Little attention, except for spherical particles (Oh, 1970), appears to have been given to erosion at impact angles other than 90°. The tangential forces that arise at lower angles and in abrasion will certainly complicate analytical studies. This observation is supported by the fact that attempts to analyze abrasive wear using lateral crack models have as yet not been as successful as those developed for erosion by perpendicular impact (Evans and Marshall, 1982).

Since we have discussed cracking under static and sliding indenters, it may be useful to review how these studies have been applied to wear prediction.

TABLE 7-1 Predicted Exponents for the Erosion of Brittle Solids

Type of Response	a	b	c	d
Elastic[a]	5	4.0		
	3.46	2.77		
Elastic[b]	4.33	3.47		
	3.3	2.65		
Elastic[c]	4.9	3.87		
	3.9	3.04	-1.33	
Elastic-plastic[d] (quasi-static)	4.0	2.4	-1.5	-0.5
Elastic-plastic[e] (dynamic)	3.67	3.16	-1.33	-0.25
Elastic-plastic[f]	3.67	2.45	-1.33	-0.11

Note: Vol ~ $R^a V^b K_{IC}^c H^d$. The exponents of R and V for elastic response are calculated for m = 5 and 15 (higher values correspond to m = 5), where m is the Weibull parameter describing the distribution of flaw sizes.
[a]Sheldon and Finnie, 1966b
[b]Oh and Finnie, 1966
[c]Oh et al., 1972
[d]Evans and Wilshaw, 1976
[e]Evans et al., 1978; Evans and Wilshaw, 1977
[f]Ruff and Wiederhorn, 1979

Erosive Wear

For the prediction of velocity and radius exponents, semi-empirical relations have been used for both static and dynamic conditions. For both

low and high indentation velocities, the material removal rate is assumed to be

$$W \sim c_\ell^2 h$$

where c_ℓ is the lateral crack length and h is the lateral crack depth below the surface. For quasi-static conditions, Evans and Wilshaw (1976) found that

$$c_\ell \sim (P/K_{IC})^{3/4} \text{ for } (c_\ell/a) > 2$$

and

$$h \sim a$$

where a is the radius of contact. The wear rate was thus obtained as

$$W \sim P^2/K_{IC}^{3/2}H^{1/2}$$

Evans and Wilshaw further found that when the resulting force is less than 10 times the threshold load, the relation between indentation load P and velocity V was

$$P/R^2G = 4.6(\rho V^2/G)^{3/5}$$

where G is the shear modulus of the indented material and ρ is the density of the indenting particle. Therefore, the wear rate for N indenting particles was taken as

$$W \sim NR^4 G^{4/5}V^{12/5}\rho^{6/5}K_{IC}^{3/2}H^{1/2}$$

For material indented with high indenting velocities, it was found that the lateral crack length was proportional to the radial crack size (Evans et al., 1978):

$$c_\ell \sim c_r \sim \gamma(RV)^{1.33}/K_{IC}^{0.66}$$

where γ is a parameter that depends weakly on the density of the indenter and indented material. The equation for lateral crack depth was derived as

$$h \sim (R^2 V\rho/H)^{1/2}$$

The wear rate was thus

$$W \sim V^{19/6}R^{11/3}\rho^{1/4}/K_{IC}^{4/3}H^{1/4}$$

Ruff and Weiderhorn (1979) obtained a different relation for lateral crack depth:

$$h \sim (\rho R^3 V^2/H)^{1/3}$$

and the equation for wear rate was obtained as follows:

$$W \sim \rho^{11/9}R^{11/3}V^{22/9}H^{1/9}/K_{IC}^{4/3}$$

Abrasive Wear

To predict volume removal in abrasive wear, several approaches have been followed. All are based on the assumption that lateral cracks are responsible for material removal. Also, it was generally assumed that the volume removal for each indenting particle could be taken as

$$\hat{V}_i = 2h_i c_i l_i$$

where l_i is the distance of motion, h_i is the lateral fracture depth, and c_i is the lateral crack length.

In the mid-1970s Evans and Wilshaw (1976) obtained a relation for lateral crack length as

$$c_\ell \sim (P/K_c)^{3/4}$$

Applying this relation to the basic model, they derived an equation for material removal for each abrasive particle as follows:

$$\hat{V}_i \propto P_i^{5/4}/H^{1/2} K_i^{3/4} l_i$$

The volume removed by N particles is then

$$\hat{V} \propto (1/K_c^{3/4} H^{1/2}) \sum_{i=1}^{N} P_i^{5/4} l_i$$

Shortly after that, Swain (1979) derived a model for material removal based on his work on scratching. From his lateral crack length equation he obtained the following equations:

$$V/l \propto H^{1/2} P^{3/2}/K^2 \quad \text{for a two-dimensional model}$$

and

$$V/l \propto P^{7/6}/K^{2/3} H^{1/2} \quad \text{for a three-dimensional model}$$

where the two-dimensional model applies for cracks occurring at the side of the slider, whereas the three-dimensional model applies for cracks occurring ahead of the slider. Based on observations of Broese van Groenou (1975), Swain concluded that voids and pores might be the major factors in forming lateral cracks ahead of the abrasive grain. In this case the three-dimensional model should apply. Swain further pointed out that in his derivation the effect of the lateral crack interactions between adjacent scratching points was not considered.

In the early 1980s, Evans and Marshall (1982) derived an equation for volume removal by applying the relations for lateral crack length and depth they obtained in their previous work. The result was as follows:

$$\hat{V}_i = \alpha_3 (\hat{P}_n{}^{9/8}/K_c{}^{1/2} H^{5/8})(E/H)^{4/5} l_i$$

The authors derived an expression for lateral crack length, c_i, under
sliding contact condition and found that it was very close to the one for
indentation. Therefore, they stated that in their approach "the influence of
the grinding morphology upon crack extension is considered to be of minor
importance."

TRIBOLOGY

Tribology is influenced by microstructural defects and irregularities
that either intersect the surface or that are near enough to the surface
to be influenced by localized surface stresses. Asperities, surface
microcracks, and surface-connected porosity are all of concern.

Surface Asperities

Surface asperities can lead to wear by both elastic and plastic mechan-
isms. The asperities result in interface contact in which the complete
applied load is supported by a very localized area. The localized stress
can be high enough to elastically initiate a crack at a pre-existing micro-
structure discontinuity. This can result in removal of the asperity or in
formation of a crack adjacent to the asperity. If the localized contact
stress on the asperity is high and essentially compressive, the asperity can
be deformed plastically. This leads to a reduction in the height of the
asperity by a smearing action and is usually accompanied by a very local-
ized, short-duration, high-temperature transient or "flash." The plastic
deformation induces residual tensile stresses in adjacent material that can
initiate subsurface cracks (referred to as lateral cracks) parallel to the
surface, leading to spalling of material after the contact has passed.
This type of mechanism occurs during the machining of ceramics and has
been documented with high-speed photography and depth-of-cut measurements
(Schneider and Rice, 1972; Hockey and Rice, 1979). Asperities also can
increase the coefficient of friction. To avoid this, ceramics for
tribological applications are usually prepared by diamond grinding and
lapping to a high level of surface finish.

Surface cracks in ceramics usually are the radial and median cracks
resulting from machining. Unmachined (as-fired) ceramics do not have these
types of cracks but generally have excessive surface roughness due to pro-
truding grains and other asperities. Because of these asperities and the
difficulty of achieving required dimensional tolerances during fabrication,
the ceramics for tribological applications generally must be machined. The
surface cracks caused by machining can be minimized by a proper sequence
of grinding. The surface is first rough-ground to a slightly oversized
dimension. Then a series of finishing steps, each subsequently with a finer

grit size of bonded or free abrasive, achieves the final dimensions and surface finish. The key is to remove the grinding damage from the prior step before going on to the next steps. Achieving a smooth surface does not assure that the median and radial cracks from the rough grinding have been removed.

Surface cracks interact with an applied stress field. A compressive stress closes the cracks, whereas a tensile stress opens them and places a stress concentration at their tip. The stress field directly under a contact load is compressive. However, at the edge of the load is a steep gradient from compressive to tensile (Hertz and Agnew, 1881). It is in this adjacent region that new surface cracks can form and existing cracks can extend (Roesler, 1956; Archard, 1953).

A static load imposes primarily compressive stresses. This closes pre-existing cracks and impedes them from propagating. Tensile stresses can occur adjacent to the contact load and at asperities, but these are generally relatively low. However, when the contact surfaces are sliding relative to each other, very high tensile stresses can occur (Smith and Liu, 1953; Hamilton and Goodman, 1966). This is illustrated in Figure 7-1.

The magnitude of the tensile stress is strongly influenced by the coefficient of friction, as shown in Figure 7-2. Gilroy and Hirst (1969) have approximated that the peak tensile stress increases exponentially to the third power of the friction coefficient

$$\frac{P_N}{P_s} = \left[1 + \frac{3\pi(4 + \nu)}{8(1+2\nu)} f\right]^3$$

where P_N is the load to cause Hertzian damage with normal loading of a spherical indentor, P_s is the load to cause surface damage with a sliding spherical indentor, ν is Poisson's ratio of the material, and f is the coefficient of friction.

Using the Gilroy and Hirst equation plus friction data from the literature (f = 0.5 for reaction-bonded Si_3N_4; f = 0.3 for sintered SiC) (Richerson et al., 1981), one can calculate that P_s is approximately $P_N/114$ for reaction-bonded silicon nitride and $P_N/34$ for sintered silicon carbide. These large stress concentrations are likely to cause elastic surface damage and wear. Reducing the coefficient of friction by surface finishing and lubrication will substantially reduce the surface stresses.

Experimental results confirm the sensitivity of ceramics to the formation of surface damage caused by sliding contact loading. For example, reaction- bonded silicon nitride test bars were exposed to stationary contact loading and to sliding contact loading with and without a solid lubricant (Richerson, 1983). The contact geometry was the same in each case. Subsequent to the contact exposure, the test bars were strength-tested in four-point bending with the prior contact region positioned in the tensile stress field opposite the interior load pins. If no contact damage was present, the strength would be comparable to control test bars, which had not been exposed to contact loading. If surface damage was present due to the

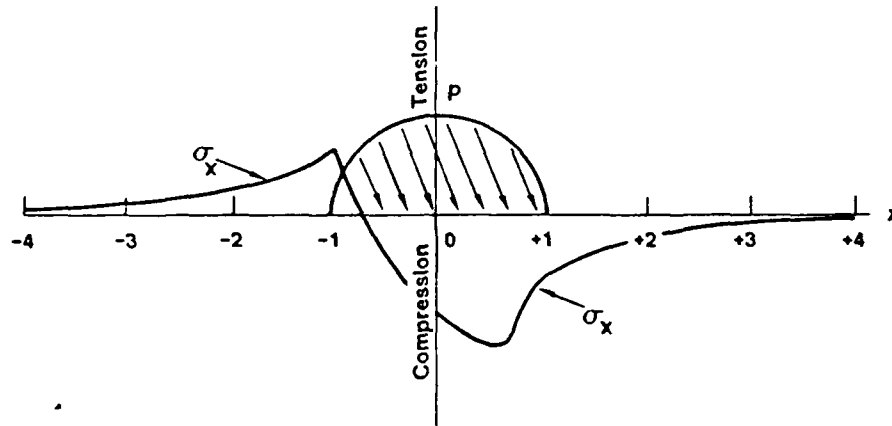FIGURE 7-1 Maximum stress σ_x at and adjacent to a sliding contact load; compressive stresses under the load, large tensile stress spike at trailing edge of load (Smith and Liu, 1953).
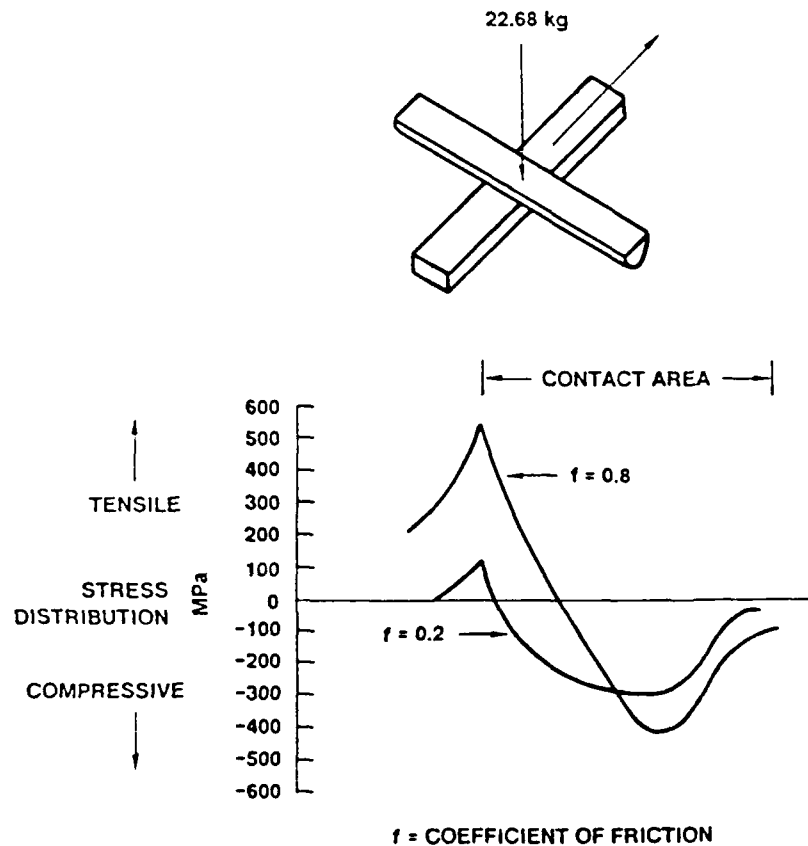

FIGURE 7-2 Effect of coefficient of friction on the magnitude of the tensile stress at the trailing edge of the sliding contact zone. Based on analysis of reaction-bonded silicon nitride data (Richerson et al., 1981).

contact loading, the strength would be lower than for the control test bars
in proportion to the increased surface crack size produced by the contact

$$S = A \left[\frac{E\gamma}{a} \right]^{1/2}$$

where S is the strength under tensile stress loading, A is a geometric
constant, E is the elastic modulus, γ is the fracture surface energy,
and a is the flaw size. For the reaction bonded silicon nitride evaluated,
the control strength of individual test bars ranged from 260 to 235 MPa. No
strength reduction occurred for static loading up to 140 kg. However, for
unlubricated sliding with a normal load of only 10 kg, large enough surface
cracks were formed to reduce the strength to 140 MPa. Use of a solid
lubricant that reduced the coefficient of friction from 0.5 to 0.2 resulted
in less surface damage and less strength decrease.

RECOMMENDATIONS

■ To provide a basis for fundamental understanding, we need to establish
a quantitative equation for the mechanical wear of ceramics. This would
include (a) a theoretical description of wear by microfracture according to
fracture mechanics and contact stress distributions, (b) a determination of
the relative importance of toughness and hardness in wear, (c) establishment
of the load dependence on wear in elastic contact and fracture, and (d) a
determination of the role of microstructure on the resistance to wear by
fracture.

■ Additional fundamental understanding also needed is a quantification
of the microfracture in wear as a function of material characteristics and
contact stress conditions. This includes (a) effect of microstructure on
fracture of the material, (b) relation of the microstructure to the scale of
the wear process, (c) relation of the scale of toughening components to wear,
and (d) stress concentration at micropores.

REFERENCES

Archard, J. G. 1953. Elastic deformation and the contact of surfaces.
Nature, Vol. 172, p. 918.

Broese van Groenou, A. 1975. Grinding of Ferrites, Some Mechanical and
Magnetic Aspects. IEEE Transactions on Magnetics, Vol. 11, No. 5,
pp. 1446-1451.

Chiang, S. S., D. B. Marshall, and A. G. Evans. 1982a. The response of
solids to elastic/plastic indentation: I--Stresses and residual
stresses. J. Appl. Phys., Vol. 53, No. 1, pp. 298-311.

Chiang, S. S., D. B. Marshall, and A. G. Evans. 1982b. The response of
solids to elastic/plastic indentation: II--Fracture initiation. J.
Appl. Phys., Vol. 53, No. 1, pp. 312-317.

Evans, A. G., and T. R. Wilshaw. 1976. Quasi-static solid particle damage in brittle solids: I--observations, analysis, and implications. Acta Metallurgica, Vol. 24, pp. 939-956.

Evans, A. G., and T. R. Wilshaw. 1977. Dynamic solid particle damage in brittle materials. J. Mat. Sci., Vol. 12, p. 97.

Evans, A. G., et al. 1978. Impact damage in brittle materials in the elastic-plastic response regime. Proc. R. Soc. London, Vol. 361, p. 343.

Evans, A. G., and D. B. Marshall. 1982. Fundamentals of Friction and Wear, p. 439. Metals Park, Ohio: American Society for Metals.

Gilroy, D. R., and W. Hirst. 1969. J. Phys. D: Appl. Pys., Vol. 2, p. 1974.

Gulden, M. 1979. Study of Erosion Mechanisms in Engineering Ceramics. Paper published under Office of Naval Research Contract No. 00014-73-C-0401.

Hamilton, G. M., and L. E. Goodman. 1966. The stress field created by a circular sliding contact. J. Appl. Mech., Vol. 33, p. 371.

Hertz, H., and J. R. Agnew. 1881. Math, Vol. 92, p. 156. (Reprinted in English in Hertz's Miscellaneous Papers, Chapters 5 and 6. London: Macmillan and Co., Ltd., 1886.)

Hockey, B. J., and R. W. Rice (eds.). 1979. The Science of Ceramic Machining and Surface Finishing. NBS Special Publication No. 562. Washington, D.C.: U.S. Government Printing Office.

Holland, A. J., and W. E. S. Turner. 1937. The effect of transverse scratches on the strength of sheet glass. J. Soc. Glass Technol., Vol. 21, pp. 383-394.

Lankford, J., and D. L. Davidson. 1979a. The crack-initiation threshold in ceramic materials subject to elastic/plastic indentation. J. Mat. Sci., Vol. 14, pp. 1662-1668.

Lankford, J., and D. L. Davidson. 1979b. Indentation plasticity and microfracture in silicon carbide. J. Mat. Sci., Vol. 14, pp. 1669-1675.

Lankford, J. 1981. Threshold microfracture during elastic-plastic indentation of ceramics. J. Mat. Sci., Vol. 16, pp. 1177-1182.

Oh, H. L., and I. Finnie. 1966. An analysis of rock drilling by erosion. Proc. 1st Cong. Int. Soc. Rock Mech., Vol. 2, pp. 99-104.

Oh, K. P. L. 1970. On the Statistical Nature of Brittle Fracture. Ph.D. Thesis in Mechanical Engineering, University of California, Berkeley.

Oh, H. L. et al. 1972. On the Shaping of Brittle Solids by Erosion and Ultrasonic Cutting, pp. 119-132. National Bureau of Standards Special Publication 348. Washington, D.C.: U.S. Government Printing Office.

Richerson, D. W. 1983. Contact Stresses at Ceramic Interfaces, pp. 657-666.
In Progress in Nitrogen Ceramics. The Hague, Netherlands: Martinus
Nijhoff Publishers.

Richerson, D. W., L. J. Lindberg, W. D. Carruthers and J. Dahn. 1981.
Contact stress effects on Si_3N_4 and SiC interfaces. Cer. Eng. and Sci.
Proc., Vol. 2, Nos. 7-8, p. 578-588.

Roesler, F. C. 1956. Proc. Phys. Soc. London, Vol. B69, p. 981 (1956).

Ruff, A. W., and S. M. Wiederhorn. 1979. Erosion by solid particle impacts.
In Treatise on Materials Science and Technology, Vol. 16. New York:
Academic Press.

Schneider, S. J., and R. W. Rice (eds.). 1972. The Science of Ceramic
Machining and Surface Finishing. NBS Special Publication No. 348.
Washington, D.C.: U.S. Government Printing Office.

Smith, J. O., and K. C. Liu. 1953. Stresses due to tangential and
normal loads on an elastic solid with application to some contact stress
problems. J. Appl. Mech., pp 157-166.

Sheldon, G. L., and I. Finnie. 1966a. On the ductile behavior of nominally
brittle materials during erosive cutting. Trans. ASME, Vol. 88B,
pp. 387-392.

Sheldon, G. L., and I. Finnie. 1966b. The mechanism of material removal in
the erosive of brittle materials. Trans. ASME, Vol. 88B, pp. 393-400.

Swain, M. V. 1979. Microfracture about scratches in brittle solids. Proc.
R. Soc. London A, Ser. A., Vol. 366, pp. 575-597.

Swain, M. V., and J. T. Hagan. 1976. Indentation plasticity and the ensuing
fracture of glass. J. Phys. D, Vol. 9, pp. 2201-2214.

Vaidyanathan, S., and I. Finnie. 1972. New Developments in Grinding,
pp. 813-831. In Grinding of Brittle Solids, M. C. Shaw (ed.).
Pittsburgh, Pennsylvania: Carnegie Press.

Weibull, W. 1939. A statistical study of the strength of materials.
Ingenioersvetenskapsakad. Handl., pp. 151-153.

CHAPTER 8

ATOMIC-LEVEL MODELING OF THE CHEMICAL AND TRIBOLOGICAL PROPERTIES OF CERAMIC SURFACES

At the heart of such technological challenges as designing the next generation of high-performance gas turbines is the critical need to solve extremely difficult tribological problems, particularly for ceramic components. To progress substantially in this endeavor it is essential to establish a microscopic atomic-level understanding of the fundamental surface processes ultimately responsible for friction, adhesion, abrasion, and wear. Both theory (quantum chemistry, simulation) and experiment (surface chemistry, surface physics) are essential in establishing this fundamental microscopic atomic-level understanding. Chemistry is a very important aspect of tribology—i.e., making and breaking of chemical bonds (adhesion, oxidation, chemical dissolution, movement of atoms, dislocations, slip planes). Elucidation of the chemistry that controls tribology should lead to completely new strategies in designing tribological systems for extreme environments.

HIERARCHY OF MODELING

A hierarchy of modeling may be established (see Figure 8-1), ranging from fundamental quantum theory (electrons and nuclei), proceeding then to atomic-level molecular dynamics and Monte Carlo simulations, and progressing through more approximate descriptions involving a continuum. This spectrum allows consideration of larger systems with longer time scales, albeit with a loss of detailed atomic-level information. At each level, the precise parameters (including chemistry and thermochemistry) of the deeper level get lumped into those of the next. The overlap between each level is used to establish these connections. This hierarchy allows motion up and down as new experiments and theory lead to new understanding of the higher levels, and new problems demand new information from the lower levels.

Critical to development of these fundamentals is a set of systems that can be prepared and studied reproducibly in different laboratories by experimental techniques capable of more detailed resolution and suitable for testing the results of theoretical modeling.

87

88

HIERARCHY OF MODELS
TRIBOLOGY
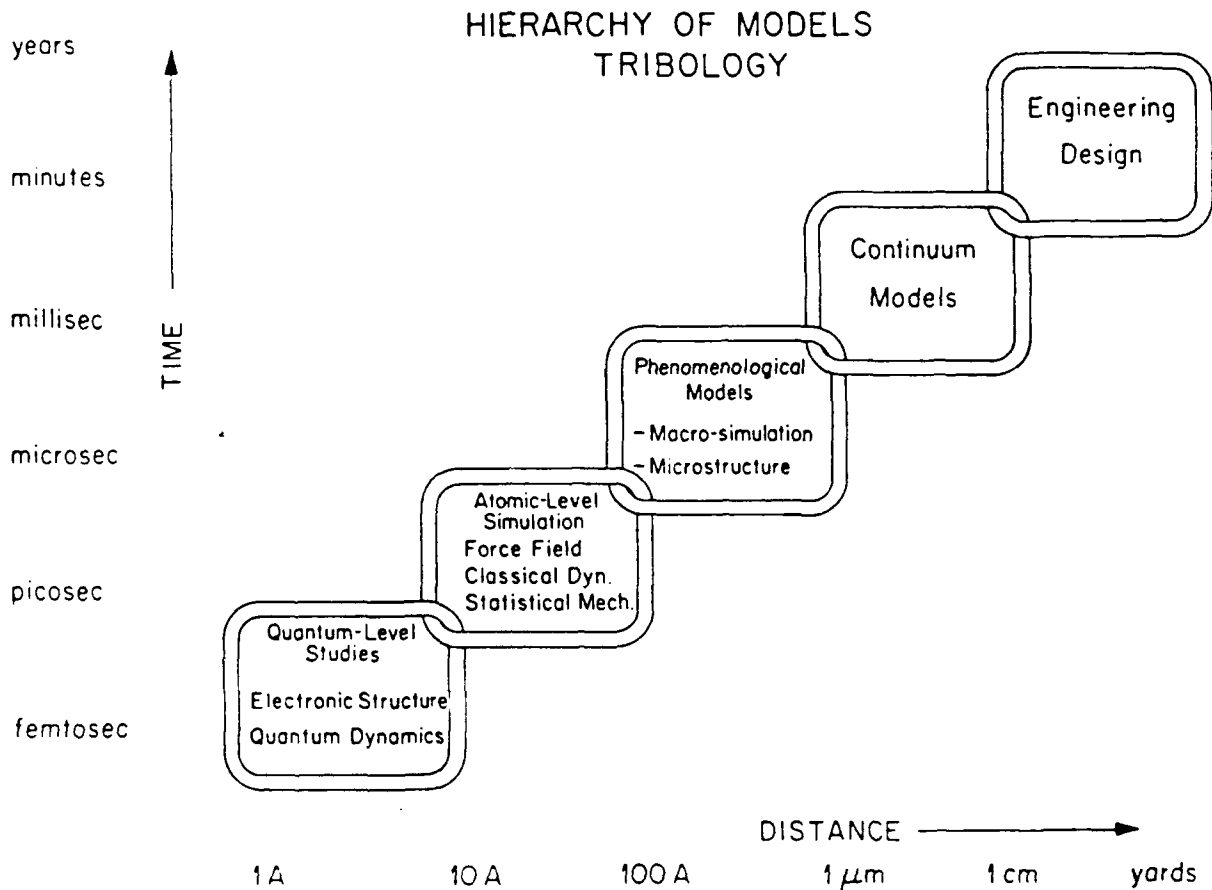
FIGURE 8-1 Relationships and connections between atomic-level descriptions of materials and the microscopic, macroscopic, and engineering models used in rationalizing experiments and designing new materials.

OUTLINE OF THEORETICAL MODELING

Although there have been rapid advances in experimental techniques for examining composition at surfaces and interfaces relevant t٠ catalysis, tribology, corrosion, and materials synthesis, there as yet is very little in the way of a microscopic theoretical model suitable for understanding the chemical, physical, and mechanical properties in terms of atomic-level structure and bonding concepts. The following approach could be taken:

1. Carry out a series of quantum chemical studies to establish the dominant surface species for clusters of atoms modeling various cٖramics and to elucidate the thermochemistry and detailed mechanistic steps involved in surface reactions of such systems.

2. Use the energy surfaces for clusters from step 1 to develop theoretical _force_ _fields_ that allow predictions of the energies and geometries for infinite surfaces and interfaces.

3. Develop procedures for molecular dynamics and Monte Carlo _simulations_ that in conjunction with the force fields from step 2 could be used to predict the rates for various diffusive and chemical processes relevant for tribology and for materials synthesis processes.

4. Interface the results of these simulations onto appropriate _graphics_ systems, allowing the designer to follow a three-dimensional image of the evolving system while interactively changing conditions and characteristics of the systems.

Through simultaneous examination of all properties of the surface (chemical, tribological, physical, and mechanical) with the same theory, there is the possibility for definitive tests on different aspects of the theory. In addition, such a central theory would provide new connections between these properties that would serve to connect what are now disconnected experiments. These theoretical developments of experimentally relevant systems should provide a level of understanding useful in designing new materials, and such computer-aided materials simulations should provide tools allowing many of the design concepts to be tested on the computer in advance of attempting difficult syntheses and characterizations in the laboratory.

Simulations of Ionic Solids

Over the past decade there has been a great deal of progress in simulating ionic solids such as halides and oxides (Catlow and Mackrodt, 1982). Thus, in a variety of systems, it has been possible to provide rather accurate predictions of the energy of formation of such point defects as vacancies (Mackrodt, 1984; Catlow et al., 1979), vacancy-interstitial pairs (Mackrodt, 1984), and substitutional impurities (Mackrodt, 1984). In addition, it has been possible to obtain useful estimates of band gaps and of donor and acceptor energies for various defects (Mackrodt, 1984).

These approaches have been used to predict rather complicated defect equilibria (e.g., vacancy clustering) (Catlow and Stoneham, 1981) and have been used to predict diffusion in ternary oxides (Dieckmann, 1984) and the detailed transport properties of fast ion conductors (Rahman, 1976; Gillan, 1983; Vashishta and Rahman, 1978). Even heavily doped systems have been treated (Catlow, 1984). For alkali halides, surface reconstruction (Tasker, 1979; Catlow et al., 1977), surface energies (Tasker, 1979), and point defects on surfaces (Mackrodt and Stewart, 1977) have also been calculated (Tasker, 1979; Catlow et al., 1977), and indeed even grain boundary properties have been predicted (Wolf, 1984). Critical to such calculations are the potentials. The most successful seem to be those of Catlow and coworkers (1977) in which empirical two-body potentials are fitted to experimental structure and elastic constants, and a simple shell model of the atomic polarizabilities is fitted to the dielectric properties. However, use of approximate theoretical ion-ion potentials (in conjunction with a shell model for polarizability) was also reasonably successful (Mackrodt and Stewart, 1979).

Despite these successes, it appears that a totally new approach will be necessary in order to attack the problems relevant to tribology of ceramics. The use of empirical two-body potentials implicitly includes the effect of three-body and higher interactions, which makes these potentials dependent upon structure being considered. Thus the F^--F^- potential in alkali-halides (Catlow et al., 1977) is significantly different from that in CaF_2 (Catlow et al., 1977). This leaves completely open the question of what to use at surfaces, grain boundaries, disordered regions, etc. In addition, for many systems of interest there will be insufficient empirical data to determine the potentials. Worse yet, many of the systems of interest are predominantly covalent (e.g., Si_3N_4, WC) and hence outside the province of the foregoing methods. However, as discussed in the following, we believe that purely theoretical methods can be used to determine all potential parameters.

Simulation of Covalent Systems

Quantum chemistry approaches have, over the past decade, led to a number of advances in the understanding of surface science and catalysis (Goddard, 1985). These studies typically involved calculating the electronic wave functions for a molecule as a function of nuclear geometry to obtain energy surfaces for ground and excited states and then examining the role of these energy surfaces for various reactions. Such quantum chemical studies will be important as the first step in examining surface configurations for various ceramic surfaces; however, to contribute to the understanding of tribology of ceramics, it will be necessary to develop methods for simulating the reaction dynamics on realistic models of these ceramic surfaces.

For the important materials questions relevant for ceramics, we must necessarily consider many thousands of atoms, and we must examine the dynamics over time scales appropriate both for chemical reactions and for diffusion. That is, we need to simulate on the computer the microscopic chemical and diffusion processes in the real system. Such simulations involve the following aspects:

1. The computer uses a general force field (describing the interactions of all particles in terms of two-, three-, and four-body forces) to evaluate the forces on all atoms at a given instant, takes the appropriate stochastic limits for nonessential degrees of freedom (describing, for example, the bulk atoms comprising the energy sink or source), and calculates the locations and velocities of the various atoms at the next time step using classical (generalized Langevin) equations of motion.

2. At appropriate time steps, a corrected set of coordinates is passed from the computer to the graphics system (see next item). The screen of the graphics system is continually refreshed with the current coordinates so that the user "sees" the reaction as it proceeds and can interactively examine the reactive system and follow the dynamics of the reaction.

3. The graphics system (with its own microprocessor and local memory so that it can rotate, translate, zoom, and window in real time) can display the whole reactive system (up to 10,000 atoms), zoom in on a selected portion of this system, and rotate and translate the view to find the critical regions.

This graphics system automatically cuts away extraneous atoms of the reactive system and automatically lets more distant atoms fade away in intensity (depth cueing). It can show the system in three dimensions (using stereo glasses coordinated with alternating left-right images on the screen) so that the user can see the reactive system as a real three-dimensional image. It automatically color-codes the atoms so that one can recognize instantly the composition and identity of the various species.

4. From the perspective of the user, he is watching the reaction as it proceeds. He can then interactively modify various parts of the system— surface structure (e.g., steps), vapor composition, atom identity, velocity (temperature) of incoming particles, bulk defects, temperature of the surface, etc.—and follow the subsequent dynamics to determine the impact of these changes upon various processes.

This overall procedure is referred to as computer-assisted materials simulation (CAMS). CAMS involves two major theoretical components:

1. Theoretical force fields (obtained from both theory and experiment) that accurately describe the forces on various atoms and molecules interacting at surfaces and with each other.

2. Theoretical methods to handle the dynamics of chemical processes within solids and on solid surfaces, including making and breaking of bonds and a description of energy dissipation.

For systems with covalent bonds, a proper description of reactions requires the explicit treatment of how bonding changes from reactant to product with the proper resonance between the forms in the transition stage region. This may require a generalization of usual force fields where spin-pairing is optimized for the electrons involved in the reacting bonds. This is a difficult problem, but several approaches seem feasible and should be tested. More serious difficulties arise in metallic systems, where the multitude of low-lying electronic states and delocalization of electrons conspire to make reliable force fields a very difficult problem indeed. Work on this is in progress, but these difficulties must be solved before progressing on metallic systems. For ceramics, however, this is not a serious issue.

This theoretical approach to force fields allows one to consider any possible combination of atoms (even when no experimental data are available) and to examine regions of the potential surface (e.g., saddle points for reactions) not readily available to experiment. It also avoids a serious problem, the interdependence of potential parameters.

An additional issue concerns the dynamics. Various groups have developed efficient classical dynamics programs (Brooks et al., 1984) that can rapidly calculate all the forces and update all coordinates and velocities—e.g., for thermolysin in H_2O (3500 atoms) it takes 33 sec on a VAX minicomputer (Olafson and Goddard, n.d.). With a good starting point (proper folding configurations), a well-optimized structure for a protein can be obtained in 600 steps (5 hours on a VAX). Unfortunately, such calculations are practical

on the molecular time scale (picoseconds), whereas many solid-state processes require consideration of long time scales (microseconds, milliseconds, or longer). As a first step in solving this problem, several groups are developing stochastic classical dynamics programs in which the active atoms (the ones undergoing reaction) are followed explicitly, but the more remote atoms are transformed away while retaining their role as a heat sink (Doll, 1978; Garrison et al., 1977; Tully, 1980 and 1981; Redondo et al., 1982 and 1984; Zeiri et al., 1984). These programs are currently being used to examine scattering (and energy transfer) of gas phase molecules on surfaces. The challenge for materials problems is to move the theory toward the diffusion time scale (Voter and Doll, 1985). This will require major new innovations, perhaps involving a combination of Monte Carlo simulation, molecular dynamics, and Langevin equations.

As should be apparent, there are enormous theoretical difficulties in developing the force fields and dynamics methodology suitable for the critical materials problems. However, there are also enormous payoffs in terms of the potential for a new level of microscopic understanding of materials processes—an understanding that should promote the development of new materials processes designed to achieve a desired microscopic structure that was pretested by computer simulation (Goddard, 1985).

STANDARD SYSTEMS FOR TRIBOLOGY

For studies of friction and wear, one could simulate moving contacts between surfaces by modeling each surface using the foregoing techniques, applying perpendicular forces of various magnitudes, and displacing the surfaces with various velocities. This should allow one to calculate first principles friction coefficients and to examine gouging and the role of defects induced under various conditions. These developments should provide a level of understanding useful in designing new materials and should provide tools allowing materials scientists to test many of the design concepts using computer graphics and the theoretical models to simulate the properties of the newly designed systems. In this way the designer should be able to refine many of the ideas in advance of attempting difficult syntheses and characterizations in the laboratory.

To make progress on the fundamentals, it is important to choose several standard systems on which various experimental and theoretical methods will be applied. In choosing these systems, the following aspects are important:

1. Experiment--Use single crystals prepared under well-defined conditions. Modify surfaces under well-controlled conditions [cleave, expose to plasmas (H_2, O_2, F_2, N_2)]. Measure friction coefficients under well-defined conditions. Measure wear under well-defined conditions. Reproducibility in different laboratories is essential.

2. Theory--Use quantum theory and molecular simulation techniques to model the same systems as studied experimentally. Predict surface structure. Predict adhesion of various adsorbates and lubricants to surfaces. Simulate friction and wear experiments.

TABLE 8-1   Standard Systems for Tribology

Material	Experimental Condition
Diamond	a. Hydrogen-saturated surface b. Fluorine-saturated surface
Graphite	a. Without H_2O or absorbed gases b. With carefully controlled amounts of rare gases (Ar, Xe) c. With carefully controlled amounts of H_2O
BN	(Oxidatively stable)
LiF	(Experiments easier because do not need UHV conditions)
CaF_2 and BaF_2	(Useful high-temperature lubricants for ceramics)
Al_2O_3	(Advantage: IR transparent for real friction experiments—e.g., W. Winer)
CoO	
MoO_3	(Basal plane)
Ag(111), (110), (100)	(Easy to clean; reconstruction not a major problem)
MoS_2	a. Orientation upon binding to various clean metal surfaces ($\mid$ versus $\parallel$ to surface) b. Effect of adsorbed overlayers on surface (H, O, S)
SiC	a. Single crystals b. CVD prepared c. Controlled dry oxidation (O_2, N_2O) and wet oxidation (H_2O)
Si(111)	(Allows very pure, very large single crystals) a. Freshly cleaved b. Saturated with hydrogen c. Controlled dry oxidation (O_2, N_2O) and wet oxidation (H_2O)
Amorphous Si: (no grains)	a. Saturation with H b. Saturation with F c. Controlled dry oxidation (O_2, N_2O) and wet oxidation (H_2O)
CVD Si_3N_4	a. As grown (oxide surface layer) b. Oxide removed and replaced with H or F c. wet- and dry-oxidized
Ni(100)	(Well-studied both by experiment and theory) a. Clean b. Sulfur covered c. Oxygen covered
Effects of doping	Particularly relevant for ceramics is the effect of doping (of ceramic or of lubricant) on adhesion of lubricant to surface
High-temperature lubricants	Worthy of study would be high-temperature oxide glasses that would be good lubricants at high temperatures (e.g., based on B_2O_3, Al_2O_3, SiO_2)

Only when these measurements have been made and theoretical models revised accordingly will prediction of friction or wear rates become feasible. Since the phenomena are so complex, predictions will always be approximations.

Some standard material systems, to be tested on like materials and with others listed, are described in Table 8-1.

RECOMMENDATIONS

To establish a basis for atomic-level simulation of the fundamental surface processes responsible for friction, adhesion, wear, and abrasion, the following is recommended:

■ A major thrust is needed in the development of theoretical methods relevant to tribology and ceramics. This would involve quantum chemistry studies of the fundamental forces in model systems, development of force fields suitable for atomic-level simulations, and simulations of realistic models and tribological systems.

■ Focus fundamental studies (both theoretical and experimental) on a series of standard systems that will serve as benchmarks for comparison between theory and experiment and between the work of different laboratories.

REFERENCES

Brooks, B. R., R. E. Bruccoleri, B. D. Olafson, D. J. States, S. Swaminathan, and M. Karplus. 1983. CHARMM: A program for macromolecular energy, minimization, and dynamics calculations. J. Comp. Chem., Vol. 4, p. 187.

Catlow, C. R. A., K. M. Diller, and M. J. Norgett. 1977. J. Phys. C, Vol. 10, p. 1395. Also Catlow, C. R. A., M. J. Norgett, and T. A. Ross. J. Phys. C, Vol. 10, p. 1627.

Catlow, C. R. A., J. Corish, K. M. Diller, P. W. M. Jacobs, and M. J. Norgett. 1979. J. Phys. C, Vol. 12, p. 451.

Catlow, C. R. A., and A. M. Stoneham. 1981. J. Am. Ceram. Soc., Vol. 64, p. 234.

Catlow, C. R. A., and W. C. Mackrodt (eds.). 1982. Computer Simulation of Solids. Berlin: Springer-Verlag.

Catlow, C. R. A. 1984. Solid State Ionics, Vol. 12, p. 67.

Dieckmann, J. 1984. Solid State Ionics, Vol. 12, p. 67.

Doll, J. D. 1978. J. Chem. Phys., Vol. 68, p. 3158.

Garrison, B. J., D. J. Diestler, and S. A. Adelman. 1977. J. Chem. Phys., Vol. 67, p. 4317.

Gillan, M. J. 1983. Solid State Ionics, Vol. 9, p. 755.

Goddard, W. A., III. 1985. Science, Vol. 227, p. 917.

Mackrodt, W. C., and R. F. Stewart. 1977. J. Phys. C, Vol. 10, p. 1431.

Mackrodt, W. C., and R. F. Stewart. 1979. J. Phys. C, Vol. 12 p. 431.

Mackrodt, W. C. 1984. Solid State Ionics, Vol. 12, p. 175.

Olafson, B. D., and W. A. Goddard, III. n.d. Molecular Mechanics Studies of Enzyme-Inhibitor Interactions: The Structure of the BAG and CLT Inhibitors Bond to Thermolysin. (Manuscript in progress; to be submitted to J. Mol. Biol.)

Rahman, A. 1976. J. Chem. Phys., Vol. 65, p. 4845.

Redondo, A., Y. Zeiri, and W. A. Goddard, III. 1982. Phys. Rev. Lett., Vol. 49, p. 1847.

Redondo, A., Y. Zeiri, and W. A. Goddard, III. 1984. J. Vac. Sci. Tech., B, Vol. 2, p. 1639.

Tasker, P. W. 1979. Philos. Mag., Vol. 39, No. 119.

Tully, J. C. 1981. Surf. Sci., Vol. 111, p. 461. Also 1980. J. Chem. Phys., Vol. 73, p. 1975.

Vashishta, P., and A. Rahman. 1978. Phys. Rev. Lett, Vol. 40, p. 1337.

Voter, A. F., and J. D. Doll. 1985. J. Chem. Phys., Vol. 82, p. 80.

Wolf, D. 1984. Philos. Mag., Vol. 49, p. 823.

Zeiri, Y., A. Redondo, and W. A. Goddard, III. 1984. J. Electrochem. Soc., Vol. 131, p. 1639.

Chapter 9

THERMOCHEMICAL ASPECTS OF THE TRIBOLOGY OF CERAMICS

Today there are essentially no theoretical guidelines for selecting
ceramic materials for tribological applications. Given the large number
of candidate ceramic materials and coatings that may be employed and the
wide compositional ranges over which many of these materials may exist, it
is extremely unlikely that ceramic sliding systems will be optimized
through exhaustive testing. Therefore, a high priority must be placed on
the development of predictive models that can estimate the performance of
ceramic tribo-systems from basic properties of materials that are widely
available or that can be measured.

There is a general agreement that all frictional and wear processes
can be accounted for on the most basic level in terms of the interactions
between the surface atoms of the contacting surfaces. Friction may be
interpreted as the surface traction that results from the interatomic
attraction at the interface.

In the case of unlubricated sliding of ceramics in a nonreactive
environment, the surface tractions can be interpreted in terms of the
interatomic attractions at the interface between the counterface materials
themselves. While such an analysis provides a useful starting point in
developing methodologies for predicting the sliding behavior of ceramic
systems, most practical ceramic components must operate under more complex
conditions. However, the primary complication in analyzing practical
ceramic systems is the identification of the species which are present at
the interface. If these are known, the same basic considerations that are
discussed herein should apply.

In particular, when new phases are formed at the interface by chemical
reaction with species in the sliding environment or by chemical reaction
with species in the sliding environment or by chemical reactions between
the counterface materials, the interatomic attractions of interest are
those between the phases that are actually present at the sliding inter-
face. When solid lubricant films are introduced at the interface, the
interfacial tractions may be limited either by the shear strength of the
film itself, in which case the interatomic bonding in the solid lubricant
controls the surface traction, or by the strength of the bonding between
the solid lubricant film and the opposing sliding surface.

The resulting surface stresses may exceed the strength of one or both of the contacting surfaces and result in the formation of wear particles through localized deformation, fatigue, and fracture of the parent materials or of surface films. There is a general correlation between the friction coefficient and the wear rate resulting from discrete particle formation, and therefore a quantitative and predictive model for the friction coefficient would be useful in the design of sliding systems.

The frictional force also results in an energy input to the interface. In the case of sliding under conditions of high speed and high load (as is normally the case, for instance, in the machining of metals with ceramic tools), the temperature rise at the interface can become significant. In this case, the mutual chemical solubilities of the sliding couple may become significant, and wear may occur primarily by dissolution on the atomic scale.

For ceramic components in high-temperature machinery, the average stress levels are usually much lower than those in machining. However, the ambient temperatures and expected lives of these components are significantly higher. While the ceramic components in the hot zones of current adiabatic engines have relatively short lives and are probably limited by mechanically activated wear processes, wear resulting from interdiffusion may be appreciable over the service life of a practical ceramic part. Since the chemical wear forms an effective lower bound for the achievable wear rate in a system of a given composition, it is desirable to develop a quantitative model that can be used for design and selection purposes.

EXISTING MODELS

In spite of the consensus concerning the relationship between the friction and wear of sliding surfaces and the atomic and/or molecular properties of the contacting materials, the quantitative modeling of friction and wear in terms of basic physical properties is in its infancy, with few available models that are useful in the design of sliding systems. This is because of the difficulty of characterizing the surface properties of materials in terms of physical properties that are easily measured and readily available to the designer. The following sections survey the current understanding of the chemical basis of the frictional and wear behavior of sliding systems for metal-metal, metal-ceramic, and ceramic-ceramic couples.

Metal-Metal Sliding Systems

A survey of the state of current understanding of the effect of the thermochemical properties of a sliding pair on its wear must start with the studies of Rabinowicz (1971) on the sliding wear of metals. Rabinowicz studied the binary phase diagrams of the metals and developed criteria for grouping the compatibilities of sliding couples in terms of the mutual solubilities of the metals comprising the sliding pair in the liquid and solid states, as shown in Figure 9-1.

Those metals that display broad miscibility gaps in the liquid state are presumed to interact weakly during sliding and generally show low wear rates. The next category shows somewhat greater interaction between the

W Mo Cr Co Ni Fe Nb Pt Zr Tl Cu Au Ag Al Zn Mg Cd Sn Pb

In
Pb
Sn
Cd
Mg
Zn
Al
Ag
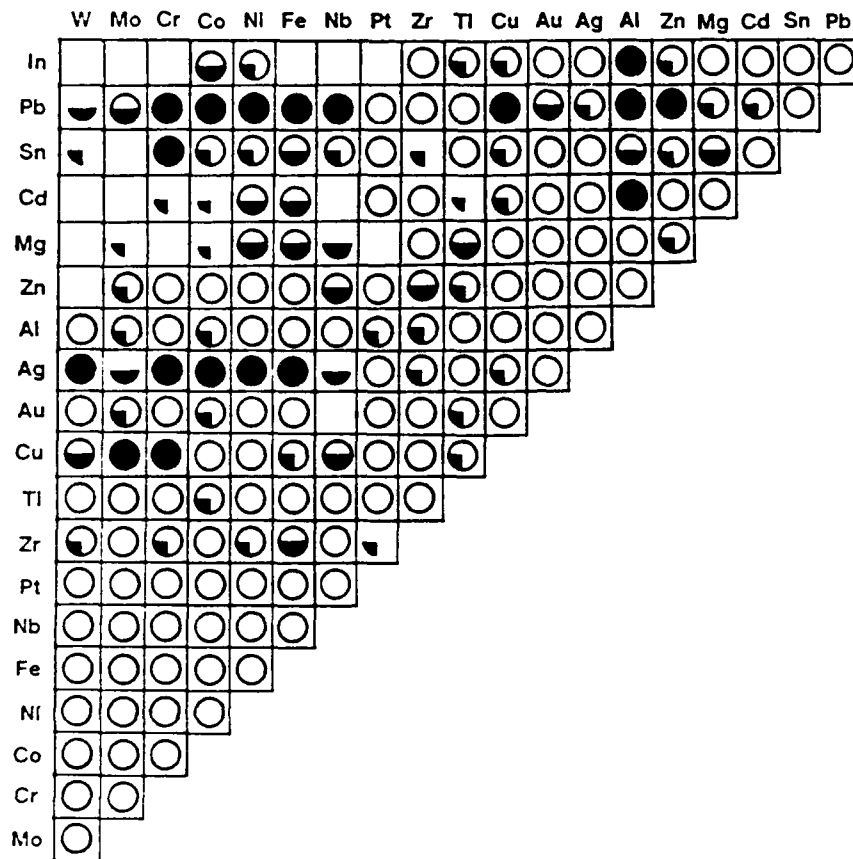Au
Cu
Tl
Zr
Pt
Nb
Fe
Ni
Co
Cr
Mo

FIGURE 9-1. Rabinowicz's compatibility chart for various metal combinations derived from binary diagrams of the respective elements in terms of preferred antifriction surfaces: ● two liquid phases, solid solution less than 0.1 percent solubility (lowest adhesion); ◒ two liquid phases, solid solution greater than 0.1 percent, or one liquid phase, solid solution less than 0.1 percent solubility (next lowest adhesion); ◓ one liquid phase, solid solution between 0.1 percent and 1 percent solubility (higher adhesion); ○ one liquid phase, solid solution over 1 percent (higher adhesion). Blank boxes indicate insufficient information. Reprinted by permission of the American Society of Lubrication Engineers.

metals and includes those that are miscible in the liquid state but show a maximum solid solubility in either solid solution phase of 0.1 atomic percent. Relatively worse wear behavior is encountered in those metals for which the solid solubility of the more soluble element is in the range from 0.1 to 1.0 atomic percent. The last category displays the most severe wear and includes those metals for which the solid solubility is in the range above 1.0 atomic percent.

While the compatibility table is a very useful design tool, it is not
a physically based model, and there are certain adjustments that must be
made. Even in the case of pure metals, the interpretation of the phase
diagrams is complicated by the formation of ordered metallic compounds that
occurs in binary alloys in which the affinity between the alloyed elements
is strong. Buckley (1980) has pointed out that the gold-silicon and gold-
germanium systems, among others, exhibit negligible solid solubility but show
relatively high wear rates. Rabinowicz developed guidelines to determine the
compatibility of those elements that form intermetallic phases in preference
to the formation of extensive solid solutions, and these have been
incorporated into his compatibility chart.

It would be preferable to construct a model that does not depend on the
experimental determination of a phase diagram for each sliding pair. This
is particularly true in the case of ceramic-ceramic or metal-ceramic systems,
where many components and phases may be present. However, the compatibility
concept has been of considerable practical use in the design of sliding
systems. In spite of the difficulties in interpreting ceramic phase dia-
grams, it might be very useful to conduct a careful and systematic study
of existing phase diagrams to see if a set of criteria similar to the
compatibility criteria for metallic elements could be developed.

Metal-Ceramic Sliding Systems

Clearly, the compatibility defined by Rabinowicz is a measure of the
chemical affinity of the two sliding surfaces. There are more quantitative
measures of chemical affinity that may be used to predict the performance
of wear components. In the case of metal-metal systems, the enthalpy of
solution of the sliding pair is an accurate measure of the chemical affinity
that might be correlated with wear performance.

For metal-ceramic systems, Miyoshi and Buckley (1982) show the dependence
of the coefficient of friction of transition metals in sliding against sil-
icon carbide as a function of the d-bond character of the metal as defined by
the Pauling resonating-valence-bond theory of metals (Figure 9-2). Although
the d-bond character seems to be a useful measure for determining the degree
of interaction of metals, it is a difficult quantity to measure with
certainty, and the applicability of the Pauling theory to ceramics with
predominately ionic or covalent bonding is not obvious.

Buckley and Miyoshi (1984) have also correlated the coefficient of
friction of Ni-Zn and Mn-Zn ferrite materials against various metals as a
function of the free energy of formation of the most stable oxide of the
metal per gram atom of oxygen (Figure 9-3). This is a more precise measure
of the degree of chemical interaction between the metal and ceramic. How-
ever, this measure ignores the contribution of the free energy balance and is
further distorted because of the differing stoichiometries of the different
metallic oxides.

A more precise chemical thermodynamic measure of the degree of inter-
action may be obtained by writing a complete and balanced dissolution
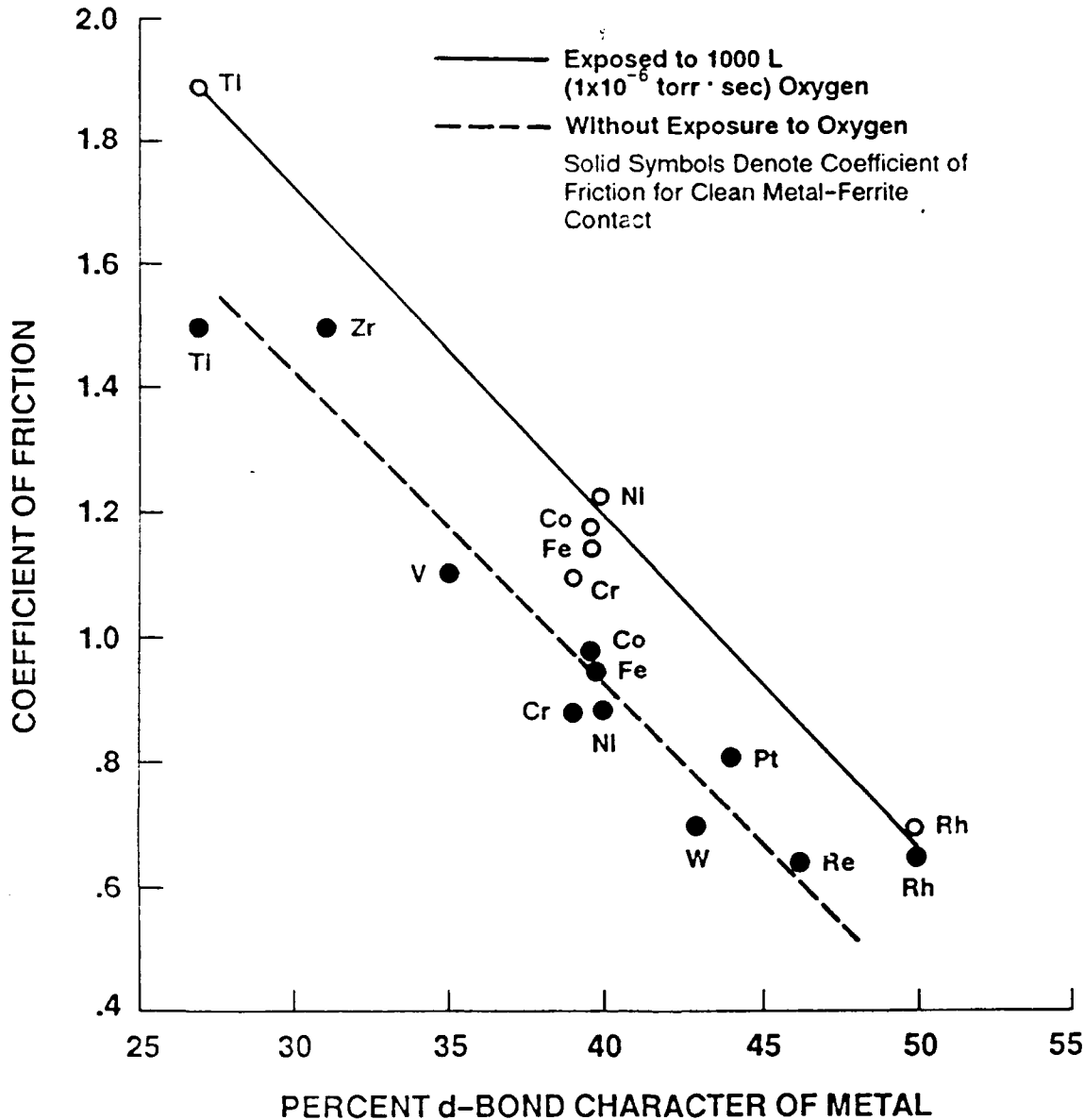reaction for a metal-ceramic sliding pair. In this case, the extent of

FIGURE 9-2 Effect of absorbed oxygen on friction for various metals in contact with the ferrites. Exposure, 1000 L in oxygen gas; sliding velocity, 3 mm/min; load, 0.05 to 0.2 N; vacuum, 3 X 10^{-8} Pa; room temperature.

dissolution of the ceramic phase in the metal or the net free energy of reaction to form new species may be taken as a quantitative measure of the affinity. Kramer and Judd (1985) took this approach in explaining the wear of ceramic cutting tool materials. These tools operate at high temperatures, and the wear of tool compositions that are based on the carbides, nitrides, and borides in the machining of most engineering metallic alloys is a direct result of the chemical dissolution process. The chemical solubility of these materials in the workpiece is, therefore, an extremely accurate predictor of
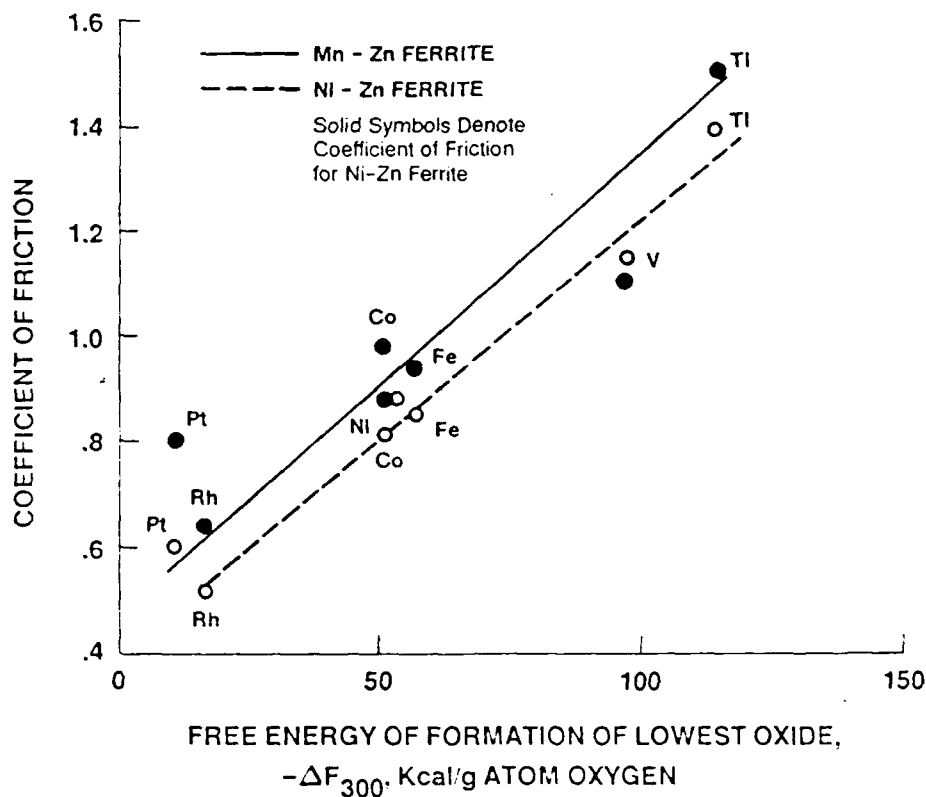
FIGURE 9-3 Coefficients of friction for various metals in contact with
ferrites as a function of free-energy of formation of lowest oxide. Single
pass sliding; sliding velocity, 3 mm/min; load, 0.05 to 0.2 N; vacuum,
3 X 10^{-6} Pa; room temperature is further distorted because of the
differing stoichiometries of the different metallic oxides.

the wear-resistance in machining. The solubility of a ceramic of composition
AxBy at a given temperature may be calculated as

$$C_{A_x B_y} = \exp \left[\frac{\Delta G_{A_x B_y} - x\Delta G_A^{-xs} - y\Delta G_B^{-xs} - RT(x\ln x + y\ln y)}{RT(x+y)} \right]$$

where

$C_{A_x B_y}$ = the solubility of the compound AxBy in the metal

$G_{A_x B_y}$ = the free energy of formation of AxBy

G_A — the relative partial molar excess free energy of dissolution of component A of the ceramic in the metal

G_B — the relative partial molar excess free energy of dissolution of component B of the ceramic in the metal

R — the perfect gas constant

T — the absolute temperature

The predicted wear rates of various ceramic materials in the machining of steel at 1300 K are shown in Table 9-1. The low wear rates predicted for the oxides are not realized in practice because, as a result of the extreme chemical stability of the oxides, mechanical wear mechanisms predominate at all practical temperatures (Huet and Kramer, 1982).

In sliding wear, the effect of temperature is more modest than in machining, and the influence of chemical affinity is felt indirectly, in terms of increased tractions between the counterface materials. Therefore, a theoretical model that yields the adhesion at the interface is required. Ferrante and Smith (1979, 1981) have attempted quantum mechanical calculations of the adhesion between metallic materials with some success, and Johnson and Pepper (1982) have employed quantum mechanical calculations to estimate the strength of metal-sapphire bonding. However, these calculations are quite difficult and involve many parameters that are not available for all common engineering materials.

The previously cited results of Miyoshi and Buckley strongly suggest that the degree of sliding wear in metal-ceramic systems can be correlated with the chemical affinity of the surfaces, as measured by the tendency toward reaction of the two phases. It would, therefore, be highly desirable to attempt to develop a theory of the sliding wear of metal-ceramic systems that is based on a more rigorous measure of the degree of chemical interaction than that which Miyoshi and Buckley used, perhaps an argument akin to that of Kramer and based on the chemical solubility of the ceramic in the metal, as defined by equilibrium theromodynamics.

Ceramic-Ceramic Sliding Systems

The extension to ceramic-ceramic systems, although more difficult because of the difficulty in identifying the actual reactions that take place, should also be feasible. In this case, the free energy of reaction of the most favorable reaction for the ceramic components may be taken as a measure of the chemical affinity.

The ultimate extension of such an analysis would result in a generalized theory of adhesion based on thermodynamic property data. Such a theory would be useful in the design of highly adherent ceramic coatings (including solid lubricant layers as well as wear-resistant coatings), metallic binders for metal-ceramic composite materials, and braze alloys for metal-ceramic and ceramic-ceramic bonding.

TABLE 9-1 Predicted Relative Solution Wear Rates of Potential
Steel-Cutting Materials at 1300 K

Potential Tool Material	Predicted Relative Solution Wear Rate, v_{wear} (HfC) = 1	Estimated Time for 25 μm of Wear
ZrO_2	0.0000367	26 months
Al_2O_3	0.00124	23 days
Ti_2O_3	0.00245	12 "
TiO_2	0.00313	9.1 "
TiO	0.0333	21 hours
HfN	0.680	60 minutes
HfC	1	41 "
ZrN	1.56	26 "
$TiC_{.75}O_{.25}$	2.86	14 "
TiN	5.92	6.9 "
ZrC	6.20	6.6 "
TaC	9.98	4.1 "
TiC (iron)	12.8	3.2 "
NbC	15.6	2.6 "
BN	57.0	43 seconds
WC	332	7.4 "
VC	381	6.5 "
Diamond	445	5.5 "
TiC (nickel)	998	2.5 "
Si_3N_4	5,440	0.45 "
β-SiC	10,700	0.23 "

Kramer, 1987

RECOMMENDATIONS

It is likely that the chemical interactions among ceramic components will ultimately determine their performance in practical applications. Therefore, given the current lack of theoretical guidance in materials selection, it is important to begin the development and evaluation of theoretical models that can be used in design. The following steps are recommended:

• Undertake a study of available metal-ceramic and ceramic-ceramic phase diagram data to develop semi-empirical compatibility criteria for ceramic materials.

• Begin to develop quantitative, analytical friction and wear models based on the chemical affinity between sliding surfaces as evaluated by chemical thermodynamic calculations.

■ Undertake test programs on well-characterized materials to provide reliable data for comparison to model predictions. Both ceramic-ceramic and metal-ceramic systems should be included.

■ Incorporate the modification of contact stresses by lubricants in the boundary, mixed and hydrodynamic lubrication regimes into theories of friction and wear.

REFERENCES

Buckley, D. 1980. Definition and Effect of Chemical Properties on Surfaces in Friction, Wear, and Lubrication. In Fundamentals of Tribology, N. Suh and N. Saka (eds.). Cambridge, Massahusetts: MIT Press.

Buckley, D., and K. Miyoshi. 1984. Friction and wear of ceramics. Wear, Vol. 100, p. 333.

Ferrante, J., and J. R. Smith. 1979. Theory of metallic adhesion. Phys. Rev. B, Vol. 19, No. 8, p. 3911.

Ferrante, J., and J. Smith. 1981. Theory of metallic adhesion. Bull. Am. Phys. Soc., Vol. 26, p. 428.

Huet, J., and B. M. Kramer. 1982. The wear of ceramic tools. Proc. 10th North American Manufacturing Research Conference, p. 297. Dearborn, Michigan: Society of Manufacturing Engineers.

Johnson, K., and S. V. Pepper. 1982. Molecular orbital model for metal-sapphire interfacial strength. J. Appl. Phys., Vol. 53, No. 10, p. 6634.

Kramer, B. 1987. On tool materials for high speed machining. Trans. ASME, Vol. 109, No. 2, p. 87.

Kramer, B. M., and P. K. Judd. 1985. Computational design of wear coatings. J. Vac. Sci. Tech. A, Vol. 3, No. 6, p. 2439.

Miyoshi, K., and D. Buckley. 1982. Adhesion and friction of transition metals in contact with nonmetallic hard materials. Wear, Vol. 77, p. 253.

Rabinowicz, E. 1971. Determination of the compatibility of metals through static friction test. ASLE Trans., Vol. 14, p. 198.

Appendix A

FOREIGN SCIENCE AND TECHNOLOGY IN
THE AREA OF CERAMIC TRIBO-MATERIALS

There is considerable worldwide interest in the use of ceramics as tribo-materials. Although the Japanese are correctly perceived to be a major participant, if not the leader, in this this field, a literature search indicates that the Germans, Russians, French, and other Europeans are also very active in the field. The Japanese apparently lead in the production of the fine ceramics required for tribological applications. The worldwide interest is spread widely across many tribological applications, including rolling element bearings, automotive engine components, seals, cutting tools, and metal-forming tools.

There appears to be an interesting difference in attitude between the Japanese and others with respect to the reasons for considering ceramics as tribo-materials. The Japanese view fine ceramics as technological materials that can be made from readily available, inexpensive raw materials and that can reduce their dependence on foreign strategic material sources. Therefore, the Japanese regard the use of ceramics as replacement materials for any tribo-application, irrespective of physical or chemical property differences. Others seem to view fine ceramics as special materials with unique qualities that may be advantageous in special applications. Thus, the Japanese appear to be pursuing the use of ceramics aggressively on a broad front whereas others are proceeding more cautiously on a special-case basis.

A literature search was conducted with the aid of H. Tischer of BAM in Berlin on the TRIBO bibliographic data base. TRIBO is the most complete bibliographic data base in tribology and is available on electronic file back to 1972. It contains about 55,000 citations. Over the past 8 years citations have been added at the rate of about 6000 per year. The country of origin is not recorded for the publication, but language of publication can give some indication in the case of non-English publications. Conclusions from such a search must be viewed with caution, but some generalizations are appropriate.

Searches were conducted on the term "ceramic(s)" and on the terms "carbide(s), nitride(s), and oxide(s)" (words only, not chemical symbols).

107

Those citations were then further sorted in three ways: (a) by year of publication to get the time trend, (b) by language of publication to infer country of origin, and (c) by type of application as "general tribo-material," "coating," or "composite." In general, these categories seemed to follow the same trends as the entire data base with respect to citations per year and distribution into language of publication. The "ceramics" accounted for just under 1 percent of the total (488 citations) and "ceramics" plus "carbides, nitrides, and oxides" accounted for about 3 percent of the total (1693 citations). The time trend of the "ceramics" citations appeared to be increasing from somewhat less than 0.5 percent in the early 1970s to about 1 percent in more recent years. The total group also was increasing with time from about 1 percent in the early 1970s to about 4 percent recently.

In terms of language of publication, the searched categories essentially paralleled the data base as a whole. Approximately half of the citations were published in English, 30 percent in German, 6 percent in Russian, 3 percent in Japanese, and 1 percent in French. The other 10 percent were in a wide variety of languages. The relative distribution between German and Japanese publications may be to some extent related to the fact that the data base originates in Germany and therefore would be expected to have a better coverage of the German-language literature than of the Japanese literature. Nevertheless, there appears to be a significant amount of information published in German in these areas. Of course, a significant number of the English-language citations originated in non-English-speaking countries. There is no easy way of determining these, however.

The citations were also examined as to category of application in terms of "coatings," "composites," and "general unspecified." For the ceramics, about 15 percent were composites and 20 percent coatings, whereas for the entire group (ceramics plus nitrides, etc.), coatings and composites each represented about a third of the whole. Curiously, fewer than 3 percent of the ceramics citations were concerned with high-temperature applications on the basis of title or key words.

Because of the many caveats associated with such a literature search and the conclusions that can be drawn from it, the numbers cited should be viewed as minimum indicators of activity in this field.

They do, however, suggest some of the activity in research and development of ceramic tribo-materials in all the major industrial countries.

Appendix B

BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS

BRIAN FROST is one of the many graduates of the University of Birmingham to move to this country. After receiving his Ph.D. degree from Birmingham in 1949 he was employed by the U.K. Atomic Energy Authority until 1969. Since then he has been at Argonne National Laboratory as Assistant Director and then Director of the Metallurgy Division, and Senior Metallurgist, Materials Science and Technology Division. Concurrent positions were Visiting Lecturer, University of London and Northwestern University. He is a fellow of the American Nuclear Society, the American Society for Metals, and the Institute of Metallurgy.

After obtaining degrees in ceramic science and engineering from the University of Utah and Pennsylvania State University, DAVID RICHERSON was employed by the Norton Co. This was followed by twelve years with the Garrett Co. in Phoenix. While there he founded and was first chairman of the Arizona section of the American Ceramic Society. Since 1985 he has held the position of Director of Research and Development of Ceramatec, Inc. In 1972 he was granted the Admiral Earle Award of the Worcester Engineering Society.

IAIN FINNIE received his B.Sc. degree from the University of Glasgow in 1949 and his D.Sc. in 1975. Additional degrees were awarded by MIT. He worked for the Shell Development Co. until 1961 after which he joined the Mechanical Engineering Department of the University of California, Berkeley. His research interests have been in the areas of creep, wear, and fracture. He is a member of the National Academy of Engineering.

After graduating from the Swiss Federal Institute of Technology where he received his Ph.D. in 1963, TRAUGOTT FISCHER taught there for six years. Following this he joined the staff of Bell Labs. Five years as Assistant Professor at Yale were followed by a research position with Exxon Research and Engineering Co. In 1986 he became professor at Stevens Institute of Technology. He is a Fellow of both the American and Swiss Physical Societies.

WILLIAM W. GODDARD, III received his undergraduate education at UCLA and his Ph.D. degree from Caltech. In 1964 he joined the Chemistry Faculty at Caltech where he is now the Charles and Mary Ferkel Professor of Chemistry and Applied Physics. He is also the Project Director of the Caltech

Materials Research Group (funded by the National Science Foundation). His early background was in engineering, but his research interests now emphasize theoretical aspects of topics ranging from reaction mechanisms in catalysis to the properties of semiconductors to the dynamics and simulation of biological and surface processes. He is a member of the National Academy of Sciences, the American Chemical Society, the California Catalysis Society, the Materials Research Society, and a Fellow of the American Physical Society.

STEPHEN HSU's B.S. degree in chemical engineering is from Virginia Polytechnic Institute. His M.S. and Ph.D. degrees are from Pennsylvania State University. Before joining the National Bureau of Standards in 1984 he worked for the Amoco Research Corporation. In 1980 he received the ASLE Alfred E. Hunt Award for the best paper of the year. In addition to the ASLE he is a member of ASME, SAE, and the American Ceramic Society.

BRUCE M. KRAMER is Professor of Mechanical Engineering at George Washington University in Washington, D.C. He earned his academic degrees at the Massachusetts Institute of Technology, where he served as Assistant and Associate Professor before joining the faculty of GWU in 1985. Professor Kramer's specialty is the quantitative modelling of the wear of ceramic materials and coatings. His work has been recognized by the FW Taylor Medal of the International Institution for Production Engineering Research, the Blackall Award of the ASME and the Bunshah Medal, an annual award of the International Conference for Metallurgical Coatings.

MILTON C. SHAW is Professor of Engineering, Arizona State University at Tempe. He received his undergraduate degree from Drexel University and received his M.ESc and Sc.D. degrees from the University of Cincinnati. From 1942-1946 he was at the NASA Flight Propulsion Laboratory (now NASA-Lewis) as Chief, Materials Branch. From 1946-1961 he was at Carnegie Mellon University as Head, Department of Mechanical Engineering and from 1974-1977 as University Professor. In 1968 Professor Shaw became a member of the National Academy of Engineering. His areas of research include tribology, materials processing, materials behavior, and engineering design.

WARD O. WINER received his B.S.E., M.S.E., and Ph.D. degrees from the University of Michigan and a Ph.D. in physics from Cambridge University in England. He was on the Mechanical Engineering faculty at the University of Michigan from 1963 to 1969. In 1969 he became Associate Professor at Georgia Institute of Technology where he is presently Regents' Professor in the School of Mechanical Engineering. He received the ASME Melville Medal in 1975; the NASA Certificate of Recognition in 1977; the Clarence E. Earle Memorial Award from NLGI in 1979; and, in 1986, the Tribology Gold Medal from the British Tribology Trust and the ASME May D. Hersey Award. He is co-editor of the ASME *Wear Control Handbook* (1980) and is Technical Editor, *ASME Transactions, Journal of Tribology*. He was on the Boards of Directors of the Society of Engineering Science, Inc. (1980-1985) and of ASLE (1982-1986). He was Chairman of the National Research Council Steering Committee on Recommendations for U.S. Army Basic Scientific Research (1984 to 1987) and is a member of the Mechanics, Structures, and Materials Engineering Advisory Committee of the National Science Foundation (1984 to present). He is also a registered Professional Engineer.